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# A Method for Measuring the Pressure in a Rubber Extruding Machine

J. H. DILLON, *Physics Division, Research Laboratory,* AND P. M. TORRANCE, *Compounding Division, Firestone Tire and Rubber Company, Akron, Ohio*

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A method for measuring the pressure exerted by rubber on the walls of the die of a tubing machine is described. An extrusion plastometer was used in these pressure measurements and the results obtained were employed in correlating the plastometer with a tube tubing machine. This was accomplished by determining the isothermal curve of efflux rate *vs.* pressure for the tubing machine and comparing with that for the extrusion plastometer. The measured values of the pressure at various speeds and temperatures of extrusion should be of value in the design of new types of extruding machines.

## INTRODUCTION

AN extrusion plastometer operating at high rates of shear of the order of magnitude of those existing in factory rubber-extrusion machines has been described elsewhere.[1] In the development of this plastometer, it was thought desirable to investigate the flow conditions existing in factory extrusion machines so as to permit reproduction of these flow conditions in the plastometer as accurately as possible. The direct measurement of temperature and extrusion rate of the tubing machine is simple. However, the measurement of the pressure exerted by the rubber on the walls of the die is comparatively difficult and, as far as the writers are aware, has not been recorded in the literature. A reasonably accurate method of measuring this pressure with the aid of the extrusion plastometer presented itself. The results are considered of value in designing new types of extrusion machines and in the calculation of shearing stresses in extrusion dies, as well as in designing laboratory testing equipment.

The plastometer, which was operated by extruding the rubber sample at a constant temperature and pressure and measuring the volume extruded in a given time, involved the same factors which control the operation of a factory tubing machine. The plastometer was designed to operate at the same average rate of shear[1] as that calculated to exist in tubing machines and should, on a theoretical basis, correlate with them. However, it was thought necessary to investigate experimentally the correlation between the plastometer and a tubing machine. Since the relation between rate of efflux and driving pressure at constant temperature is a fundamental criterion of the flow conditions in an instrument or machine, it was decided to determine that relation for a tubing machine and compare the form of the resulting curve with that which is found to hold for the extrusion plastometer.[1]

The direct measurement of this pressure in a tubing machine, by means of moving piston or diaphragm devices, is made difficult because of the tendency of uncured rubber to work into very small crevices and thus cause undesirable friction in the moving parts of the measuring device. The pressure can be calculated from measurements of the thermo-mechanical efficiency of the tuber but is subject to unavoidable errors of $\pm 100$ percent or more. The indirect measurement of the pressure in a tubing ma-

[1] Dillon and Johnston, Physics **4**, 225 (1933); Rubber Chem. Tech. **7**, 248 (1934).

TABLE I. *Measurement of pressure in tube tubing machine. (Tube stock A.)*

| NO. | SCREW SPEED (r.p.m.) | TEMP. OF TUBES (°C) | TEMP. OF FEED (°C) | TUBE WEIGHT (g/cm) | BELT SPEED (m/min.) | TUBE EFFLUX RATE ($cm^3$/min.) | DIE DESIG-NATION | 1/8" DIE EFFLUX RATE ($cm^3$/min.) | PRESSURE IN TUBES (kg/$cm^2$) | PRESSURE TO GIVE SAME EFFLUX RATE AT 105.4°C (kg/$cm^2$) | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *A* 1 | 36.2 | | | 4.42 | 9.45 | 3940 | L | 192 | | | |
| 2 | | | | | | | B | 113 | | | |
| 3 | | | | | | | L | 198 | | | |
| 4 | 36.6 | 85.0 | 48.6 | 4.77 | 9.60 | 4330 | B | 113 | | | |
| 5 | | | | | | | L | 203 | 122 | 105 | |
| 6 | 36.6 | | | 5.00 | 9.45 | 4450 | B | 125 | 97 | 86 | |
| *B* 7 | 39.1 | | | 4.88 | 9.15 | 4210 | L | 216 | | | |
| 8 | | | | | | | B | 132 | | | |
| 9 | 38.3 | | | 5.24 | 8.85 | 4300 | L | 208 | | | |
| 10 | | | | | | | B | 135 | | | |
| 11 | 38.8 | 86.3 | — | 5.12 | 8.85 | 4270 | L | 209 | | | |
| 12 | | | | | | | B | 138 | | | |
| 13 | | | | | | | L | 220 | 124 | 107 | |
| 14 | | | | | | | B | 144 | 102 | 91 | |
| *C* 15 | 41.4 | | | 5.12 | 9.45 | 4570 | L | 246 | | | |
| 16 | | | | | | | B | 173 | | | |
| 17 | 41.1 | | | 5.23 | 9.60 | 4750 | L | 245 | | | |
| 18 | | | | | | | B | 168 | | | |
| 19 | 41.1 | 86.0 | | 5.23 | 9.45 | 4660 | L | 234 | 138 | 112 | |
| 20 | | | | | | | B | 173 | 116 | 98 | |
| *D* 21 | 47.3 | — | | 5.00 | 10.2 | 4820 | L | 217 | | 108 | Conveyor |
| 22 | | | | | | | B | 184 | | 101 | stopped |
| *E* 23 | 47.5 | | | 5.00 | 10.2 | 4820 | L | 220 | | | Set-up |
| 24 | | | | | | | B | 216 | | | stock |
| 25 | | | | | | | L | 204 | | | used to |
| 26 | | | | | | | B | 204 | | | start run |
| 27 | 46.9 | 94.0 | | 5.23 | 10.2 | 5040 | L | 208 | 104 | 106 | New oper. |
| 28 | | | | | | | B | 189 | 102 | 103 | |
| *F* 29 | 56.3 | | | 5.00 | 11.3 | 5330 | L | 250 | | | |
| 30 | | | | | | | B | 204 | | | |
| 31 | 56.0 | 94.6 | 51.6 | 5.00 | 11.5 | 5400 | L | 251 | | | |
| 32 | | | | | | | B | 194 | | | |
| 33 | 56.3 | | | | | | L | 249 | | 114 | |
| 34 | | | | | | | B | 194 | | 104 | |
| *G* 35 | 61.1 | | | 5.23 | 12.8 | 6350 | L | 275 | | | |
| 36 | | | | | | | B | 210 | | | |
| 37 | | | | | | | L | 259 | | | Feed |
| 38 | | | | | | | B | 216 | | | shortage |
| 39 | 61.1 | 99.2 | — | 5.23 | 12.8 | 6350 | L | 270 | 118 | 118 | |
| 40 | | | | | | | B | 215 | 108 | 107 | |
| *H* 41 | 74.3 | | | | 14.0 | 6950 | L | 290 | | | |
| 42 | | | | | | | B | 227 | | | |
| 43 | | | | | | | L | 302 | | | |
| 44 | | | | | | | B | 220 | | | |
| 45 | 74.5 | | | | | | L | 315 | | | |
| 46 | 74.6 | 105.4 | | 5.23 | 13.7 | 6780 | B | 235 | | | |
| 47 | | | | | | | L | 304 | | | |
| 48 | | | | | | | B | 238 | | | |
| 49 | | | | | | | L | 326 | 122 | 122 | |
| 50 | | | | | | | B | 258 | 109 | 109 | |
| *I* 51 | | | | | | | L | 371 | | | |
| 52 | | | | | | | B | 257 | | | |
| 53 | 89.9 | | | 5.00 | 16.0 | 7580 | L | 371 | | | |
| 54 | | | | | | | B | 269 | | | |
| 55 | 89.2 | 112.1 | | 5.46 | 16.3 | 8410 | L | 405 | | | |
| 56 | | | | | | | B | 289 | | | |
| 57 | | | | | | | L | 402 | 134 | 137 | |
| 58 | | | | | | | B | 297 | 115 | 121 | |
| *J* 59 | 89.0 | 112.3 | | 5.12 | 17.1 | 8260 | L | 382 | | | Set-up |
| 60 | | | | | | | B | 302 | | | |
| 61 | 89.1 | | | 5.00 | 16.6 | 7850 | L | 353 | 128 | 130 | |
| 62 | | | | | | | B | 244 | 102 | 103 | |

chine by the use of the extrusion plastometer, as herein described, was not subject to the objections applying to the other two methods.

## Apparatus

No complicated apparatus was required for this experiment. The tuber which was used in the experiments was of the twin-screw type, with water-cooled barrel and screws; a special tube die illustrated in Fig. 1 was constructed. It was of conventional design except that there were inserted in the walls two circular dies 3.18 mm (1/8″) in diameter (*L* and *B*, as shown in Fig. 1). These dies were of exactly the same size and shape as the die used in the extrusion plastometer.[1] That extrusion plastometer was the only other apparatus necessary for the pressure measurement.

## Procedure

A representative set of data is given in Table I. The speeds of the drive motor and of the belt upon which the tubed rubber was carried across the rollers of a continuous reading Toledo scale were measured by means of a tachometer. The temperature of the tubes and feed rubber were measured by inserting a preheated mercury-in-glass thermometer into a large roll of the hot rubber stock and observing the maximum readings. The linear weight of the tubes was measured with a Toledo scale provided in the tubing equipment. Tube efflux rate was simply belt speed multiplied by linear weight. The efflux time for the 3.18 mm (1/8″) dies was obtained by the use of a stopwatch. After weighing the extruded rubber, the efflux rate was computed.

The dies *B* and *L* were mounted so that the rubber was deflected from its normal channel at a point 2.3 cm from the tube orifice. The exact geometry of the situation is evident in Fig. 1. It should be noted that the short cylindrical channel leading up the 3.18 mm (1/8″) dies is of the same diameter, 1.27 cm (1/2″), as the piston of the extrusion plastometer.

Summation of the efflux rates from the two 3+ mm dies, in the data of Table I, shows that the rubber stock extruded from both 3+ mm dies is about 8 percent of that from the tube die on the average. Hence, the flow from the 3+ mm dies should not seriously perturb the flow from the tube die. To verify this conclusion, die *B* was used alone at the beginning of a run. Then, without making any other change, the plug was removed from die *L*, and flow was started from *L*. No decrease in tube weight was observed.

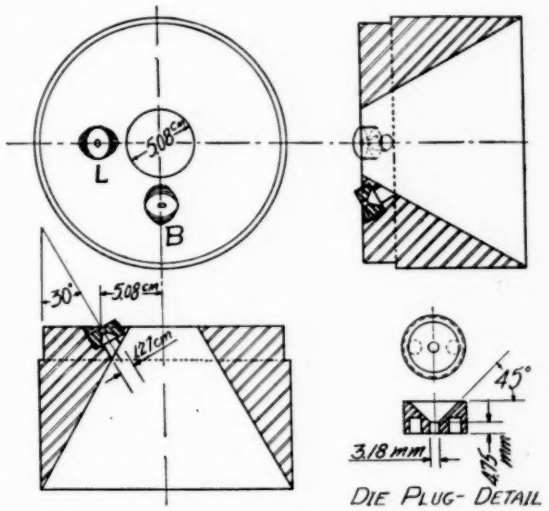


Fig. 1. Special tube die (scale drawing).

The equations of state for the tubing machine and extrusion plastometer, respectively, may be written:

$$F(E, T, P, S) = 0, f(e, t, p, s) = 0; \text{ where}$$

$E$ = efflux rate from inner tube die,
$e$ = efflux rate from 3.18 mm (1/8″) die,
$P$ = pressure at inner tube die,
$p$ = pressure at 3.18 mm (1/8″) die (of plastometer),
$T$ = temperature at inner tube die,
$t$ = temperature at 3.18 mm (1/8″) die (of plastometer),
$S$ = set-up factor at inner tube die,
$s$ = set-up factor at 3.18 mm (1/8″) die (of plastometer).

For a given stock in the extrusion plastometer, run at a temperature at which set-up (premature vulcanization) does not occur, $e$, $t$, $p$ can be determined directly. For a higher temperature at which set-up occurs in the plastometer, the set-up factor $s$ can be eliminated by taking $e$ *vs.* $t$ curves and extrapolating the curves to the desired temperature. To ascertain what the true shape of the $e$ *vs.* $t$ curve is with $s$ eliminated, a batch of tube stock *A* and a batch of the same stock with accelerator omitted (Stock *B*) were mixed on the experimental 30.5 cm (12″) mill. In Fig. 2, the full line curves for stock *A* show

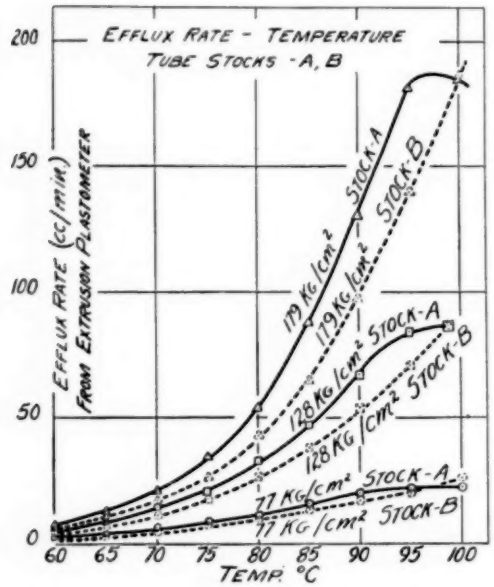


FIG. 2. Efflux rate from extrusion plastometer as a function of temperature and pressure. Tube stocks—*A*, *B*.

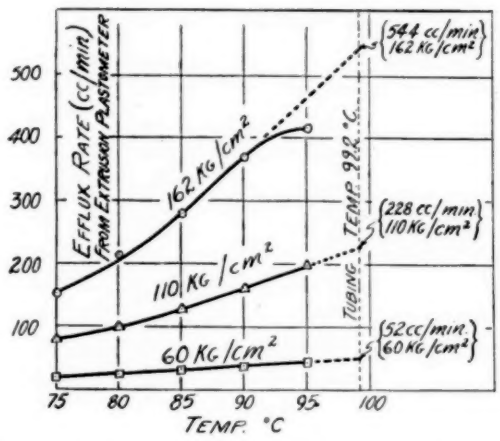


FIG. 3. Efflux rate from extrusion plastometer as a function of temperature and pressure. *G*-tubed sample taken from tuber.

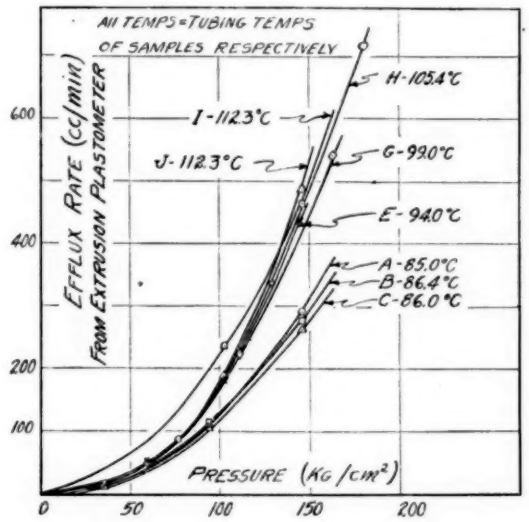


FIG. 4. Efflux rate from extrusion plastometer as a function of pressure. Tube stock *A*, tubed samples taken from tuber. Samples *A*, *B*, *C* run at temperatures recorded on curves. Curves for *E*, *G*, *H*, *I*, *J*, samples obtained by extrapolation of $E-T$ curves.

set-up starting at 90°C for the curves run at $p=77$ kg/cm² (1090 lbs./in.²) and $p=128$ kg/cm² (1820 lbs./in.²), and at 95°C for the curves run at $p=179$ kg/cm² (2540 lbs./in.²). The dotted line curves for the unaccelerated stock *B* approach linearity at the higher temperatures. Thus, a linear extrapolation of the curves for the accelerated stock *A* should give the values of *e*, with *s* eliminated. It should be emphasized that the difference between the ordinates of the curves below the set-up temperature for *A* and *B* at a given pressure is due to the softening action of the accelerator.

After *s* is eliminated as described above, we have a complete knowledge of *e*, *t*, *p* for a given tube stock. The efflux rate from the tuber *E* and the temperature of the extruded stock *T* may be determined directly, but the pressure in the tubing machine is unknown and must be determined indirectly by the use of an instrument in which the extrusion pressure is measured as a function of efflux rate and temperature. The extrusion plastometer[1] was well adapted to this purpose and was employed as follows:

Data such as those of Table I are obtained, and tubed samples are taken for the several speeds of tubing employed. These tubed samples are plied up and *e vs. t* curves are run with them in the plastometer. A sample set of these curves is given in Fig. 3. Five such sets of curves were necessary for analysis of the data of Table I, but only one set is given, in order to save space in this journal. These curves are extrapolated (when necessary) to the temperature at which the respective samples were tubed and, from the three (*e*, *p*) points thus determined, the true *e vs. p* curves (set-up eliminated) are plotted in Fig. 4.

Now in the *G*-curve of Fig. 4, for example, the pressure corresponding to the efflux rate *e* for

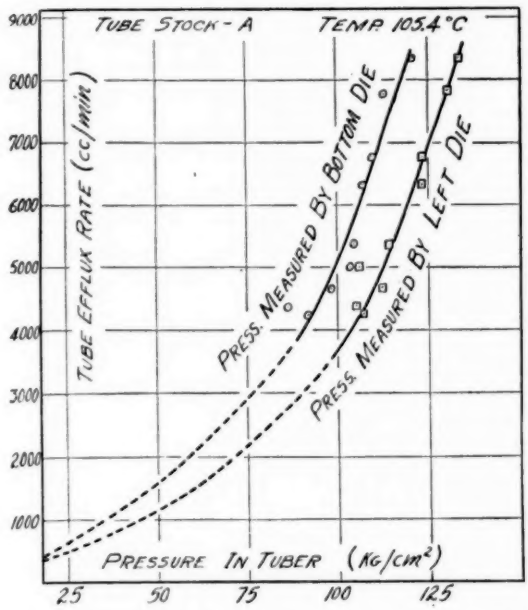


FIG. 5. Efflux rate as a function of pressure in twin screw tuber.

the bottom 3.16 mm (1/8″) die of the tuber at $T=t=99°C$ ($e=214$ cm³/min.) is read from the curve. Thus the pressure in the tuber is seen to be 108 kgm/cm² (1540 lbs./in.²). Similarly, the pressures corresponding to the other tubing states are obtained from the other curves of Fig. 4. These values of $P$ are the actual values, existing in the tuber at existing temperatures and speeds.

Sufficient data have now been obtained to permit comparison of the flow conditions in the plastometer and tubing machine die. This is accomplished by plotting an isothermal $E$ *vs.* $P$ curve which represents the flow conditions in the tube die. Thus, we read from the curves of Fig. 4 the values of the pressure $P$ (see Table I) which would be necessary to give the observed efflux rate $e$ at 105.4°C (a typical tubing temperature). The value of $E$ corresponding to this value of $e$ is then read from Table I and $E$ plotted against $P$ in Fig. 5. This extrapolation is correct only if the assumption is made that $E(T)$ is of the same form as $e(t)$. However, for the small range of temperatures here observed, this assumption appears quite justified. These extrapolated values of $P$ are given in Table I and are plotted as abscissas in Fig. 5.

All the foregoing experiments and analyses finally yield the two curves of Fig. 5. These curves give the flow conditions at the left and bottom, respectively, of the die of this particular tuber.

The lines drawn through the points of Fig. 5 approach the $P$-axis at points far to the right of the origin. Unfortunately, the tuber could not be operated at lower speeds which would yield points on the part of the curve near the origin. Still, it should be remarked that, within the region in which it was possible to obtain data, the $E$ *vs.* $P$ curve for the tuber closely resembles that which obtains in the extrusion plastometer.[1] Thus it seems reasonable to assume that the flow conditions in the tuber are of the same type as those in the extrusion plastometer. The pressures are seen to be consistently higher at the left die than at the bottom die. This result is in agreement with experience with the twin screw tuber.

The objection might be raised, that the set-up $S$ taking place in the tuber has not been determined or eliminated. This is not an objection, for it is desired to find the $E$ *vs.* $P$ curve for the tuber under the conditions employed for production of tubes. Set-up effectively changes the stock as we go to faster rates of tubing. Furthermore, the tuber screws exert a large plasticizing action, which tends to counteract the stiffening effects of set-up. The tuber, operating at different speeds, effectively operates on a series of stocks differing slightly in plasticity. The curves of Fig. 5 include the effect of set-up and the plasticizing action of the screws. They are thus "practical efflux rate *vs.* pressure curves."

## CONCLUSION

This method of measuring the pressure at the die of the tubing machine obviously gives only approximate absolute values, but it gives quite accurate relative values. The method has the advantage of not requiring complicated and delicate measuring apparatus in the tuber. It is simple from an experimental standpoint, although it does require a few graphical calculations. It should be noted that this method would apply equally well to a tread tuber.

The authors wish to thank N. Johnston for helpful criticism, and N. A. Shepard under whose direction this work was done.

# Rheological Properties of Asphalt *

## II. Discussion of Penetration-Viscosity Relationships

R. N. TRAXLER, C. U. PITTMAN AND F. B. BURNS, *The Barber Asphalt Company, Maurer, N. J.*

(Received December 3, 1934)

Although a simple exponential type of equation such as that given by Saal and Koens may give an approximation suitable for many practical purposes, it does not relate the viscosity and penetration of asphalts with the accuracy warranted by the experimental data. An accurate correlation would require a much more complicated equation which would be of doubtful practical value. Asphalts obtained from different sources or those prepared or processed differently require distinctly characteristic constants in the equation proposed by Saal and Koens. This is true no matter whether the change in consistency is due to variations in the temperature of testing or in the method or extent of processing. An asphalt brought to a given penetration by regulating the temperature does not necessarily have a viscosity identical with that of the same type of asphalt having that penetration at a different temperature.

THE methods and apparatus available at present for determining the rheological properties of asphalts at atmospheric temperatures are unsuitable for use in a control laboratory because of the time and care required to obtain accurate results. Consequently, until some rapid but reliable method is perfected, it appeared desirable to establish for viscous asphalts some relationship which would permit the calculation of their viscosity from the results of some standardized test. Obviously, the test must be dependent upon the viscosity and must be easily, quickly, and accurately made in a control laboratory. Of all the tests commonly used to evaluate asphalts, the penetration[1] seemed to be the best because fairly satisfactory results can be obtained over a rather wide range of consistency.

Saal[2] and Saal and Koens[3] have given some data on the penetration and viscosity of asphalts. For the viscous bitumens used they obtained the relationship

$$\eta = (5.13 \times 10^9)/P^{1.93}, \qquad (1)$$

where $\eta$ = viscosity in poises, and $P$ = penetration obtained with a load of 100 grams applied for 5 seconds. The reader might conclude from these two papers that Eq. (1) is applicable to all viscous asphalts. However, it must be realized that the equation was developed from penetration-viscosity data on only two asphalts which apparently were produced from the same oil by the same process. The viscosity and penetration were varied by changing the temperature at which the determinations were made.

### PENETRATION-VISCOSITY DATA OBTAINED BY VARYING THE TEMPERATURE

In a previous paper[5] the viscosities of five viscous asphalts were given at various temperatures within the range 15 to 130°C. At the time that these data were obtained, penetrations were determined over a part of this range. These results were obtained with a load of 100.00 plus or minus 0.01 gram applied for five seconds to a needle which had been checked against one certified by the U. S. Bureau of Standards; the samples were immersed in a bath containing water at the desired temperature. In order to minimize personal errors as much as possible, five or six determinations were made by at least two operators and averaged to give the results reported. The viscosities at 35°C and below were determined by the method of Bingham and Stephens[4] and at 40°C by the modification of the Bingham-Murray Plastometer described in a previous paper.[5] Each of the viscosity values is the average of ten or more determinations made at different shearing stresses. In all of the experiments the temperature was maintained within plus or minus 0.1°C.

* I. appeared in Physics **5**, 221 (1934).

[1] A.S.T.M. Method D5–25.

[2] R. N. J. Saal, Proceedings World Petroleum Congress, London **II**, 515 (1933).

[3] R. N. J. Saal and G. Koens, J. Inst. Petroleum Techn. **19**, 176 (1933).

[4] E. C. Bingham and R. A. Stephens, Physics **5**, 217 (1934).

[5] C. U. Pittman and R. N. Traxler, Physics **5**, 221 (1934).

Each of the asphalts used was from a different source and had a penetration of approximately 60 at 25°C, 100 grams, 5 seconds. Asphalt *A* was produced from a Mexican petroleum from the Panuco field by steam distillation in a batch still; *B* in the same manner from a heavy gravity petroleum from the Mene Grande field in Venezuela; *C* similarly from a petroleum from the Island of Trinidad. *D* was made by softening refined Bermudez Native Lake Asphalt with an asphaltic flux of 45 seconds float at 66°C produced by steam distillation of the petroleum used in the production of *B*; *E* was made from refined Trinidad Native Lake Asphalt by softening with the same flux as used in making *D*. The characteristics of these asphalts together with the viscosities and penetrations at various temperatures are given in Table I.

TABLE I. *Viscosities and penetrations at various temperatures.*

| *T*°C | Penetration 100/5 | Viscosity-poises |
|---|---|---|
| | *Asphalt A*—R & B softening point 52°C<br>Ductility at 25°C—100+cm | |
| 15 | 26 | $9.20 \times 10^7$ |
| 20 | 42 | $2.26 \times 10^7$ |
| 25 | 62 | $6.98 \times 10^6$ |
| 30 | 94 | $2.75 \times 10^6$ |
| 35 | 137 | $8.45 \times 10^5$ |
| 40 | 199 | $2.33 \times 10^5$ |
| | *Asphalt B*—R & B softening point 52°C<br>Ductility at 25°C—100+cm | |
| 15 | 23 | $6.33 \times 10^7$ |
| 20 | 41 | $1.760 \times 10^7$ |
| 25 | 61 | $6.24 \times 10^6$ |
| 30 | 97 | $1.806 \times 10^6$ |
| 35 | 148 | $4.97 \times 10^5$ |
| 40 | 234 | $1.713 \times 10^5$ |
| | *Asphalt C*—R & B softening point 48°C<br>Ductility at 25°C—100+cm | |
| 15 | 16 | $6.49 \times 10^7$ |
| 20 | 32 | $1.472 \times 10^7$ |
| 25 | 60 | $3.35 \times 10^6$ |
| 30 | 107 | $9.02 \times 10^5$ |
| 35 | 178 | $2.50 \times 10^5$ |
| 40 | 291 | $8.06 \times 10^4$ |
| | *Asphalt D*—R & B softening point 50°C<br>Ductility at 25°C—71 cm | |
| 15 | 19 | $3.69 \times 10^7$ |
| 25 | 61 | $3.66 \times 10^6$ |
| 30 | 97 | $1.277 \times 10^6$ |
| 35 | 152 | $4.91 \times 10^5$ |
| 40 | 240 | $1.276 \times 10^5$ |
| | *Asphalt E*—R & B softening point 52°C<br>Ductility at 25°C—85 cm | |
| 15 | 23 | $4.32 \times 10^7$ |
| 20 | 40 | $1.245 \times 10^7$ |
| 25 | 62 | $4.06 \times 10^6$ |
| 30 | 110 | $1.323 \times 10^6$ |
| 35 | 169 | $4.84 \times 10^5$ |
| 40 | 267 | $1.376 \times 10^5$ |

When the penetration-viscosity data given in Table I were plotted to rather condensed log-log scales, they appeared to be well represented by straight lines which were distinctly different for each asphalt. However, when the equations of these lines were established and the viscosities calculated by substituting the experimental values of the penetrations, about one-third of the calculated viscosities were found to deviate from the experimental by at least fifteen percent. When these data were plotted to more expanded scales, it was found that the line connecting the experimental points for any given asphalt was actually a sinuous curve. An examination of a similar plot of the data of Saal and Koens[3] showed curves of essentially the same type. The addition of a sine term of constant amplitude and frequency to the linear logarithmic relationships which were established gave somewhat better agreement between the calculated and experimental values. When a sine term of constant amplitude and varying frequency was added, the agreement was no better than with the simpler expression. Neither of these correction terms reduced the deviations sufficiently to warrant their use. Thus, such a simple equation as that given by Saal and Koens can be used only when a rough approximation of the viscosity is desired. Furthermore, no single equation will fit all types of asphalts; consequently, any relationship used must be calculated from data obtained in the laboratory for each particular kind of bitumen used.

## PENETRATION-VISCOSITY DATA FROM DIFFERENT CONSISTENCIES OF THE SAME TYPE OF ASPHALT

While a knowledge of the change in viscosity with temperature is very important, fully as necessary is information concerning the change in viscosity of any given type of asphalt with processing. The results of Saal and Koens,[2, 3] which were obtained on only two viscous asphalts, are insufficient to determine whether the penetration-viscosity relationship obtained by changing temperature would coincide with that obtained by a difference in degree of proc-

essing. From some of our preliminary work this appeared unlikely. To settle the question, several consistencies of three different types of asphalt were used in further experiments at 25.0 plus or minus 0.1°C. The penetrations were obtained in the same manner as described above and the viscosities were determined by the Bingham-Stephens method.[4]

The series of asphalts used are designated *D*, *E* and *G*. Series *D* and *E* were prepared by fluxing refined Bermudez and Trinidad Native Lake Asphalts, respectively, to various consistencies with the flux described above for making Asphalts *D* and *E*. Series *G* was prepared in a batch still by steam distillation of a mixture of heavy gravity with some medium gravity petroleum from the Mene Grande field in Venezuela; the samples were all taken from the same still run at different time intervals in order to obtain the different consistencies. The characteristics of the various asphalts in the three series together with the viscosities are listed in Table II.

TABLE II. *Characteristics of series D, E and G.*

| Asphalts | R & B softening point | Ductility at 25°C cm | Penetration 25°C 100/5 | Viscosity-poises at 25°C |
|---|---|---|---|---|
| D–1 | 61°C | 36 | 19 | $4.13 \times 10^7$ |
| D–2 | 59 | 42 | 23 | $2.43 \times 10^7$ |
| D–3 | 55 | 58 | 39 | $8.44 \times 10^6$ |
| D–4 | 51 | 69 | 58 | $4.24 \times 10^6$ |
| D | 50 | 71 | 61 | $3.66 \times 10^6$ |
| D–5 | 49 | 74 | 70 | $2.46 \times 10^6$ |
| D–6 | 46 | 83 | 96 | $1.272 \times 10^6$ |
| E–1 | 62°C | 34 | 23 | $2.43 \times 10^7$ |
| E–2 | 59 | 46 | 29 | $1.493 \times 10^7$ |
| E–3 | 54 | 74 | 50 | $4.92 \times 10^6$ |
| E–4 | 53 | 79 | 56 | $4.37 \times 10^6$ |
| E | 52 | 85 | 62 | $4.06 \times 10^6$ |
| E–5 | 48 | 99 | 82 | $1.636 \times 10^6$ |
| E–6 | 47 | 100+ | 93 | $1.229 \times 10^6$ |
| G–1 | 62°C | 26 | 32 | $1.805 \times 10^7$ |
| G–2 | 56 | 100+ | 45 | $8.77 \times 10^6$ |
| G–3 | 53 | 100+ | 55 | $5.28 \times 10^6$ |
| G–4 | 49 | 100+ | 83 | $1.748 \times 10^6$ |
| G–5 | 46 | 100+ | 110 | $9.01 \times 10^5$ |
| G–6 | 41 | 100+ | 174 | $3.61 \times 10^5$ |

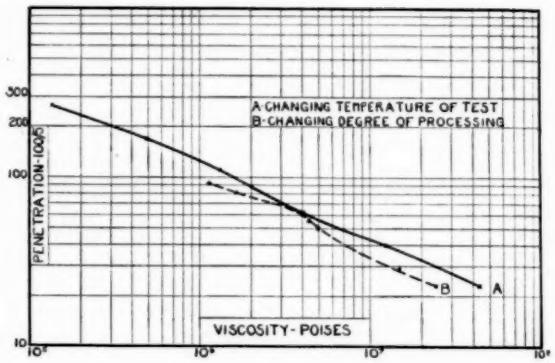


FIG. 1. Log-log plot for Asphalt *E* and series *E* showing correlation between penetration and viscosity measurements.

By analyzing the data in Table II in the same manner as those in Table I, a similar type of sinuous curve was obtained for each series. Again the addition of the sine terms discussed above gave poor agreement between experimental and calculated values of viscosity.

Fig. 1, which is a log-log plot of the data for Asphalt *E* and series *E*, was drawn to show the difference between the effect of temperature variation and of processing on the penetration-viscosity relationship. The same divergency was noted for Asphalt *D* and series *D*. Consequently, penetration-viscosity relationships obtained by varying the temperature of testing cannot be applied to a series of asphalts in which the consistency is varied by altering the extent and degree of processing.

Although the asphalts used in this work were to some degree thixotropic, the above data were obtained only after it was certain that the structure had been broken down.

The authors are indebted to Mr. H. E. Schweyer for the drawing.

# Ostwald Viscometers for Petroleum Oils

EUGENE WILLIHNGANZ, *The School of Chemistry and Physics, The Pennsylvania State College*

(Received September 26, 1934)

A series of modified Ostwald viscometers is described. They are shown experimentally to have a time of flow that is proportional to the kinematic viscosity when they are used with petroleum oils of a viscosity between 2.17 and 1280 centistokes.

RECENTLY it was desired to determine the viscosity of mineral oils to better than one-half of one percent. Examination of the Saybolt instrument showed that results of this accuracy could not be obtained in routine work because of unavoidable variations in tubes and in the technique of handling them. The size sample required was an additional disadvantage of this type of instrument. Of the other methods of determining the viscosity, the Ostwald pipette appeared the most promising, but work with a commercially available form of this instrument showed that it was no more satisfactory than the Saybolt instrument.

This led to a study of the design of the Ostwald type of viscometer. As a result of this study, instruments were built which are convenient and sufficiently rugged for general use and which were found experimentally to give results reproducible to within 0.2 percent when they were used for routine work. It is to be noted that these instruments were tested and used with mineral oils only and that they will give erroneous results with a fluid whose surface tension is different from that of the mineral oil unless they are calibrated with such a fluid. In addition they are useful only for liquids which have a viscosity greater than that of water. For liquids that have a viscosity approximately equal to, or less than that of water, the Bingham instrument is still to be preferred.

Conditions influencing the design of viscometers of the Ostwald type have been reviewed by Barr.[1] In the light of his discussion, the instrument shown in Fig. 1 has the following disadvantages:

(A) The straight U shape is sensitive to a slight tilt so that the results are not exactly reproducible.

(B) The kinetic energy correction is not known and is difficult to determine.

(C) The constriction above the upper bulb traps liquid. When air is sucked past this liquid, an added resistance is introduced to the flow of the oil.

(D) The lower bulb is so small that a slight difference in filling changes the effective head. This effective head also changes with temperature.

(E) The upper bulb is small and so shaped that part of the oil adheres to the wall, and the amount of oil left in the bulb may vary with the surface tension and the viscosity of the oil.

(F) The effective head is so small that it varies with the surface tension of the coil.

It is possible, but not practical, to design an instrument for which all of these objections have been made negligible in all cases. In the special case of an instrument which is to be used exclusively for mineral oils, the problem is

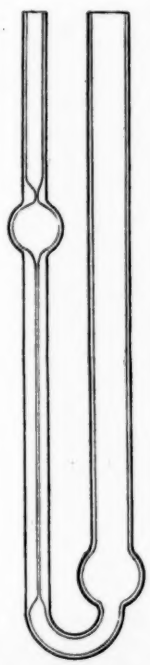

FIG. 1. Ostwald viscosity pipette.

[1] Guy Barr, *Monograph of Viscometry*, Oxford University Press, 1925.

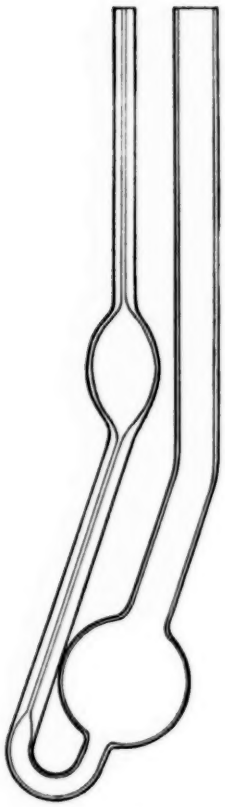

FIG. 2. Viscometers of the 100, 200 and 300 series.

FIG. 3. Viscometers of the 100A series.

simplified considerably, and the instruments shown in Figs. 2 and 3, and described in Table I are free from objections. For instruments of this design, the change of head with temperature can be allowed for, the drainage error may be determined experimentally and eliminated by the choice of a suitable volume and shape of the bulb, and the other sources of error can be shown by direct calculation to be negligible if the viscometer is calibrated with mineral oils. Under these conditions the time of flow is directly proportional to the viscosity, i.e., $\eta = T/K$. For instruments of the 100A, 200 and 300 series (see Table I) $K$ was found to be independent of the viscosity over the entire useful range of the instruments. These three instruments cover the entire range of viscosities of lubricating oils that are of interest.

TABLE I. *Dimensions of viscometers for mineral oils.*

| Viscometer series No. | 100A | 100 | 200 | 300 |
|---|---|---|---|---|
| Sample size, cc | 15 | 5 | 5 | 5 |
| Upper bulb volume cc | 10 | 2.5 | 2.5 | 2.5 |
| Diameter of lower bulb cm | 3 | 3 | 3 | 3 |
| Capillary length, cm | 7 | 7 | 7 | 7 |
| Capillary diameter cm | | | | |
| above upper bulb | 0.012 | 0.012 | 0.012 | 0.016 |
| below upper bulb | 0.007 | 0.007 | 0.012 | 0.016 |
| Viscosity range | | | | |
| Centistokes | 4.6–45 | 4.6–45 | 40–400 | 125–1250 |
| Saybolt | 41–200 | 41–200 | 185–1800 | 560–5500 |

The 100 series of instruments covers the same range of viscosities as the 100A, but is considerably more rugged and convenient and uses only a 5 cc sample. It is therefore included in spite of the fact that it has a drainage correction. This correction can be included in the pipette constant for which typical values are shown in Fig. 4.

The 200 and the 300 series instruments have constants which are independent of the viscosity. In this respect they differ from instruments of the 100 series. When a 2.5 cc working volume is used, it seems surprising to find that the viscous oils have no drainage correction while the lighter oils do, but this observation has been checked with a large number of viscometers and no

exception has been found. The shape of the curve shown in Fig. 4 shows that the change of value of $K$ is not caused by a kinetic energy correction, and an examination of the individual terms of Poiseuille's law shows that it must be a drainage error.

In all of these viscometers the value of $K$ depends on the temperature. If the instrument is calibrated at 100°F the constant at any other temperature may be calculated from the equation:

$$K_t = K_{100}(1 + V(D_{100}/D_t - 1)/\pi r^2 h).$$

In this equation $V$ is the total volume of oil in the viscometer, $D$ is the density, $h$ is the effective head, $r$ is the radius of the lower bulb. For instruments of the 100, 200 and 300 series, the equation becomes: $K_{210} = 1.005K_{100}$, where $K_{210}$ is the constant at 210°F.

In using these viscometers it is desirable to limit the individual sources of error to 0.1 percent. To do this it is necessary to control the experimental conditions within the following limits:

| | |
|---|---|
| Temperature | 0.05°F (0.03°C) |
| Stopwatch error | 3.6 sec. per hour |
| Sample volume | 0.05 cc |
| Tilt of viscometer | 2.5°. |

These conditions are easily met. The instruments are set vertical by hanging a small plumb-bob in the large arm of the viscometer. The watches used must be checked, a well regulated thermostat must be used, the viscometer must be clean, and dust must be removed from the oil. For the removal of dust, a sintered glass filter has been found convenient.[2]

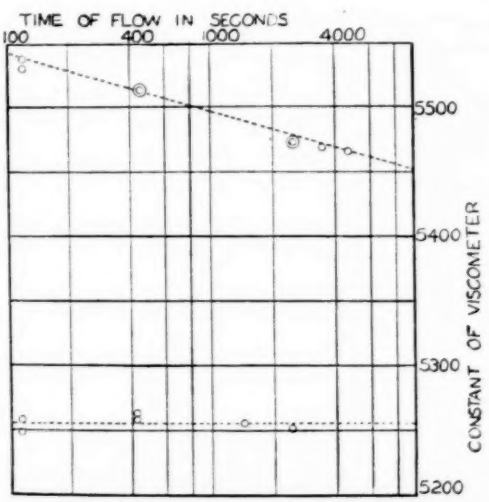


FIG. 4. Calibration curves of a typical 100 and 100A viscometer.

To calibrate these viscometers it is necessary to have a series of oils of known viscosity. Such oils may be obtained from the Bureau of Standards, but their viscosity is stated to be accurate to only 1 percent while for this work, a precision of 0.1 percent was desired. Oils of approximately the desired viscosities were therefore prepared, and their viscosities relative to water were measured. The results were expressed as kinematic viscosity, and were based on a value of 1.0078 centistokes (1.005 centipoises) for water at 20.00°C.

Of the instruments for measuring the relative viscosities of water and oil, that of Washburn and Williams[3] appeared to be most satisfactory. The drainage error of this instrument is small since it has a large working volume. The surface tension correction may be calculated, the kinetic energy correction measured, and if the instrument is always clamped in a vertical position, the other sources of error are negligible.

The kinetic energy correction of this instrument was found by determining the time of flow of water, first under the usual conditions, and then when a measured external pressure was applied. The average effective head[4] was then determined by a graphical integration.

After this viscometer had been calibrated and used to measure the viscosities of the lighter oils, the heaviest of these oils was used to calibrate a viscometer similar to that of Washburn but modified to make it suitable for heavier oils. The essential difference consisted of a larger capillary, and a slightly larger working volume. In addition, the upper bulb was placed directly above the lower one. This new viscometer was then used to determine the viscosities of four heavy oils.

This gave a series of eight oils whose viscosity relative to water had been determined. They were used to calibrate the small viscometers

[2] A. H. Thomas, Philadelphia, Pa., Cat. No. 5593.
[3] Washburn and Williams, J. Am. Chem. Soc. **35**, 737 (1913).
[4] Dorsey, J. Opt. Soc. Am. **14**, 45 (1927).

(100, 200 and 300 series) over their entire working range. The results of such a calibration are shown in Fig. 4, and have already been referred to. The consistency of the results is a further check on the performance of the Washburn, and the modified Washburn instruments. As a final check on the entire calibration, the viscosities of the oils supplied by the Bureau of Standards were measured with these small viscometers. The results of these measurements are given in Table II, and show that the instruments give satisfactory results.

TABLE II. *Results of the examination of the standard viscosity samples of the Bureau of Standards.*

| Oil No. | Temp. °F | Visc. No. | Kinematic viscosity | Absolute viscosity in centipoises Found | Given |
|---|---|---|---|---|---|
| 6F | 100 | 301 | 286.7 | 272.2 | 272 ±3.0 |
| 4 | 100 | 115 | 64.55 | 56.16 | 56.6 ±0.5 |
| | 100 | 118 | 64.99 | 56.55 | |
| | 100 | 118 | 64.99 | 56.55 | |
| | 100 | 220 | 64.53 | 56.14 | |
| 1A | 100 | 220 | 17.19 | 14.34 | 14.4 ±0.1 |
| | 100 | 115 | 17.20 | 14.35 | |
| | 100 | 118 | 17.11 | 14.26 | |
| 4 | 210 | 115 | 7.294 | 6.086 | 6.05 ±0.05 |
| | 210 | 115 | 7.275 | 6.067 | |
| | 210 | 118 | 7.277 | 6.072 | |
| | 210 | 105 | 7.273 | 6.065 | |
| 1A | 210 | 115 | 3.640 | 2.900 | 2.87 ±0.03 |
| | 210 | 118 | 3.626 | 2.889 | |
| | 210 | 105 | 3.632 | 2.894 | |

It is a pleasure to express my appreciation to the staff of the Petroleum Refining Laboratory of the Pennsylvania State College for their friendly cooperation, and especially to Professor M. R. Fenske who supervised the work, and to W. B. McCluer who suggested the effect of tilt. It is also a pleasure to express my appreciation to the Pennsylvania Grade Crude Oil Association who generously supported this work.

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FEBRUARY, 1935 PHYSICS VOLUME 6

# The Association by the Fluidity Method of Substances Which are Solid at Ordinary Temperatures

EUGENE C. BINGHAM AND JAMES E. HATFIELD,[1] *Lafayette College, Easton, Pennsylvania*

(Received January 2, 1934)

The fluidities of mixtures of benzoic acid and naphthalene with benzyl benzoate have been measured to show that it is possible to estimate the fluidity and association of benzoic acid and naphthalene below their melting points in a variety of ways; first, by using the undercooled liquid; second, by extrapolating the fluidity curve of the liquid; third, by extrapolating from a mixture to the pure substance in the undercooled state, and possibly in several solvents; fifth, by measurement of the various derivatives of the compound and extrapolating the association back to the mother substance; or, sixth, by measurement of other homologs in the same series, and extrapolating to the desired member. In this paper the last method is shown to be the most satisfactory. How far the method may be extended remains to be seen. Some such method must be resorted to in estimating the fluidity and association of substances which cannot be obtained in the fluid condition at the temperatures at which the fluidity is desired. The authors predict the fluidity curves of oxalic and malonic acids in the anhydrous form. The first does not melt before decomposing and the second is unstable. The method makes it desirable to obtain values of the association for representatives of the different classes of chemical compounds. The method may then be of practical use in obtaining the molecular weights of substances of very high molecular weight, particularly of substances of high association.

## Introduction

TO test the possibilities of the protection theory it is desirable to measure the association of certain substances which are solids at ordinary temperatures. (1) These substances may not liquefy at any convenient temperature as in the case of aminoacetic acid, acetamide and oxalic acid yet knowledge of the association of the undercooled liquid may be desired. (2) They may decompose as in the case of malonic acid and rubber or: (3) The association of a solid below its melting point may be required.

With crystalline solids there is *first* of all the possibility of measuring the fluidity in the under-

[1] Master's thesis of Lafayette College.

cooled state. The method was applied to water by White and Twining[2] down to −7°C. It has been employed many degrees below the melting point in the case of substances like benzophenone and it is obviously applicable to substances which resemble glass or resins over a wide range of temperature. Very viscous substances like glycerol or glycerol trinitrate are well-known examples of substances which exist for long periods of time in the undercooled condition. A more intensive study will show that a large number of compounds may be obtained in the undercooled condition. It is, however, difficult at times to obtain conditions which will permit fluidity measurements in the undercooled state without trouble from crystallization.

A *second* method of obtaining the fluidity is to determine the fluidity curve over a considerable range of temperature above the melting point. It is then possible to extrapolate into the undercooled state. This method is applicable to easily melting solids but it is inapplicable in the case of oxalic acid or of malonic acid or rubber.

A *third* method depends upon making solutions of varying concentrations and determining the fluidity-volume concentration curve. It may then be possible to extrapolate this so as to obtain the fluidity and therefrom the association of the pure substance. This method is applicable to many difficult cases such as rubber and malonic acid where the substance is unstable at high temperature. The difficulty is to obtain a solvent which will give a sufficiently high concentration of solute so that any possible solvation between the solid and the solvent will not interfere.

But if indirect methods such as the above are to be used, they will be much safer to use if they can be confirmed by other methods of an independent nature. One very simple variation is to change the solvent. Although the change seems slight, it may from a chemical point of view be very important.

*Fifth*, it is possible to approach the problem quite differently. It has been shown elsewhere that the association of chemical substances is closely related to the chemical constitution. Since it is possible to measure the fluidity of succinic, glutaric, adipic acids, it seems possible to extrapolate the association curve and in that way obtain the association and consequently the fluidity of both malonic and oxalic acids. This method obviously would have quite wide applications, since it would enable one to supply the wide gaps in our present knowledge.

A *sixth* method resembles the last, but instead of using other acids, in order to get the association of one acid, *e.g.*, oxalic acid, it is proposed to obtain the fluidity of various esters or other derivatives of the acid in question which are capable of measurement.

## Apparatus and Materials

Experience has shown that above 100°C it is difficult to obtain the accuracy which is readily obtained from 0° to 100°. Mineral oils volatilize, darken, and the expense makes a small bath necessary; even liquids such as tricresyl phosphate darken and give off unpleasant vapors at temperatures below 250°C. To obtain greater accuracy and safety a new bath was built.

The bath was 15 cm square on the inside and 28 cm deep constructed of sheet brass 0.32 cm thick on the sides and 0.64 cm on the bottom. It was rivetted together and brazed. At a distance from the outside of 4 cm, another box of brass was made around the first and the space filled with Silocel. A hole in the outer box at the bottom allowed heat to be added by means of a gas burner. At the front and back of the bath at a convenient height a plate glass window, 8 cm square, was inserted to permit a view of the marks on the viscometer and thermometer. The bath was very well stirred and it was set up under a hood. It could be heated by either electricity or gas. Two pieces of thick plate glass were held in the bath at right angles to the two windows so that the light passing through the bath would pass almost the entire distance through glass. This made it possible to see the marks on the viscometer readily even when the liquid of the bath was much darkened. The source of light behind the bath was a 100 watt lamp. This bath was used up to above 230°C. It was necessary to avoid rubber about the frame of the viscometer and for packing, asbestos and glass wool were found satisfactory.

[2] White and Twining, J. Am. Chem. Soc. **50**, 380 (1913).

TABLE I. *Summary of fluidities and specific volumes of compounds measured.*

| T | FLUIDITY | V |
|---|---|---|
| | BENZOIC ACID | |
| 121° | 66.93 | 0.9151 |
| 130 | 75.35 | 0.9231 |
| 140 | 85.00 | 0.9319 |
| 150 | 95.15 | 0.9387 |
| | BENZOIC ACID 75% BENZYL BENZOATE 25% | |
| 110° | 59.10 | 0.9231 |
| 120 | 67.99 | 0.9307 |
| 140 | 86.70 | 0.9464 |
| | BENZOIC ACID 50% BENZYL BENZOATE 50% | |
| 100° | 52.05 | 0.9108 |
| 120 | 70.47 | 0.9294 |
| 140 | 88.89 | 0.9480 |
| | BENZOIC ACID 25% BENZYL BENZOATE 75% | |
| 80° | 39.91 | 0.9140 |
| 100 | 54.57 | 0.9227 |
| 120 | 73.80 | 0.9320 |
| 140 | 92.34 | 0.9501 |
| | BENZYL BENZOATE | |
| 5° | 5.18 | 0.8818 |
| 15 | 8.24 | 0.8890 |
| 25 | 12.06 | 0.8958 |
| 40 | 19.07 | 0.9058 |
| 60 | 30.68 | 0.9200 |
| 80 | 44.56 | 0.9283 |
| 100 | 60.39 | 0.9454 |
| 120 | 81.96 | 0.9613 |
| 140 | 99.70 | 0.9764 |
| | NAPHTHALENE | |
| 80° | 102.56 | 1.0193 |
| 100 | 127.87 | 1.0385 |
| 120 | 154.08 | 1.0515 |
| 140 | 184.16 | 1.0860 |
| 150 | 203.65 | 1.0987 |
| | NAPHTHALENE 75% BENZYL BENZOATE 25% | |
| 80° | 86.50 | 0.9992 |
| 100 | 108.45 | 1.0103 |
| 120 | 132.45 | 1.0226 |
| 140 | 160.25 | 1.0343 |
| | NAPHTHALENE 50% BENZYL BENZOATE 50% | |
| 70° | 63.13 | 1.0004 |
| 80 | 72.56 | 1.0015 |
| 100 | 92.51 | 1.0037 |
| 120 | 116.01 | 1.0059 |
| 140 | 140.68 | 1.0081 |
| | NAPHTHALENE 25% BENZYL BENZOATE 75% | |
| 53° | 36.40 | 1.0134 |
| 60 | 40.56 | 1.0104 |
| 80 | 56.88 | 1.0095 |
| 100 | 75.58 | 0.9966 |
| 120 | 95.69 | 0.9899 |
| 140 | 118.06 | 0.9832 |
| | DIMETHYL OXALATE | |
| 60° | 97.46 | 0.8535 |
| 80 | 127.43 | 0.8788 |
| 100 | 160.51 | 0.9154 |
| 120 | 194.94 | 0.9249 |
| 140 | 233.50 | 0.9451 |
| | DIETHYL OXALATE | |
| 0° | 30.65 | 0.8488 |
| 10 | 39.58 | 0.9137 |
| 20 | 49.60 | 0.9242 |
| 30 | 60.70 | 0.9350 |
| 40 | 72.70 | 0.9461 |
| 60 | 98.40 | 0.9687 |
| 80 | 130.38 | 0.9930 |
| 100 | 163.93 | 1.0183 |
| 120 | 198.02 | 1.0449 |
| 140 | 236.96 | 1.0729 |
| 160 | 282.48 | 1.1025 |
| | *n*-DIPROPYL OXALATE | |
| 0° | 20.65 | 0.9562 |
| 10 | 27.64 | 0.9637 |
| 20 | 35.60 | 0.9748 |
| 30 | 44.72 | 0.9834 |
| 40 | 54.76 | 0.9953 |
| 60 | 77.33 | 1.0185 |
| 80 | 103.54 | 1.0446 |
| 100 | 132.64 | 1.0616 |
| 120 | 171.24 | 1.0789 |
| | SUCCINIC ACID | |
| 190° | 40.70 | 0.8378 |
| 210 | 55.74 | 0.8464 |
| 220 | 64.47 | 0.8477 |
| 230 | 73.15 | 0.8535 |
| | GLUTARIC ACID | |
| 100° | 6.55 | 0.8265 |
| 120 | 11.21 | 0.8405 |
| 140 | 17.12 | 0.8507 |
| 160 | 25.64 | 0.8755 |
| 180 | 35.58 | 0.8786 |
| 200 | 46.72 | 0.8917 |
| | ADIPIC ACID | |
| 160° | 22.11 | 0.8685 |
| 172 | 27.57 | 0.9085 |
| 183 | 32.62 | 0.9233 |
| 193 | 37.92 | 0.9333 |

TABLE II. *Associations and fluidities of various substances.*

| Substance | Association | Rhes |
|---|---|---|
| (1) Benzoic acid | 1.778 | 100 |
| (2) Benzyl benzoate | 1.131 | 100 |
| (3) Naphthalene | 1.264 | 200 |
| " | 1.254 | 100 |
| (4) Dimethyl oxalate | 1.477 | 100 |
| " " | 1.425 | 50 |
| (5) Diethyl oxalate | 1.362 | 100 |
| " " | 1.24 | 50 |
| (6) *n*-Dipropyl oxalate | 1.334 | 100 |
| " " | 1.16 | 50 |
| (7) Succinic acid | 2.290 | 50 |
| (8) Glutaric acid | 2.153 | 50 |
| (9) Adipic acid | 2.070 | 50 |
| (10) Malonic acid | [2.46] | 50 |
| (11) Oxalic acid | [2.65] | 50 |

The viscosity of water at 20°C was assumed to be 1.005 cp. Three viscometers were used, No. 1–23, $C=1.360\times10^{-7}$, $m_l=0.53$, $m_r=1.57$; No. 7, $C=11.81\times10^{-6}$; No. 1–28, $C=2.083\times10^{-7}$. The densities were measured on pycnometer No. 1-31 and on a form suggested by Sugden.[3] Benzyl benzoate was redistilled, melting at 18.5°C, boiling point 324°. Benzoic acid was sublimed, melting at 121.7°C, from J. T. Baker Chemical Company, naphthalene was sublimed, melting at 79.5°C from J. T. Baker Chemical Company; malonic acid, melting at 132°C, succinic acid, melting at 187°C, boiling at 234°C; glutaric acid, melting at 97.4°C; adipic acid, melting at 149.2°C; dimethyl oxalate, boiling at 163°C; diethyl oxalate 184.5°C; *n*-dipropyl oxalate boiling at 209°C. These acids were obtained from Eastman Kodak Company. The glutaric acid, melting at 93.8°C, boiling point 302.5°C, adipic acid, melting at 149°C, boiling at 205.5°C and dimethyl oxalate, melting at 52.2°C, boiling at 163.2°C were distilled under reduced pressure.

## DATA

In Table I are given the fluidities and specific volumes obtained, and in Table II are given the associations at the fluidity stated in the table.

## DISCUSSION

### Benzyl benzoate and benzoic acid mixtures

In Fig. 1 there is plotted the fluidity-volume concentration curve for benzoic acid and benzyl benzoate mixtures at 120°C, with the use of volume percentages. Pure benzoic acid at this temperature is a solid but the figure illustrates how it is possible to obtain the fluidity by extrapolation with satisfactory results. Since however benzoic acid melts at 121°C, it is quite permissible to extrapolate the fluidity temperature of pure benzoic acid which is given in Fig. 2 as an almost linear curve, No. 5.

In examining these curves, it may be remarked that benzyl benzoate ($C_{14}H_{12}O_2$) has the higher fluidity, although benzoic acid ($C_7H_6O_2$) has a much lower molecular weight. This anomaly is due to a much higher association on the part of the latter, caused by the unprotected carboxyl group of the acid. Compare this with acetic acid

[3] Sugden, *The Parachor and Valency*, Routledge and Sons.

($n=1.9$), and ethyl acetate 1.2 for the same phenomenon. The curves of the mixtures are sagged indicating a slight tendency of the two compounds to form a union between them, the deviation from the linear curve at all temperatures indicating 1 mole of benzoic acid to 1.1 to 1.2 moles of benzyl benzoate. The complex is therefore probably $C_{14}H_{12}O_2$. $C_7H_6O_2$.

### Naphthalene and benzyl benzoate mixtures

Napthalene and benzyl benzoate give no indication of solvate formation, the fluidity-volume percentage curves, Fig. 3, being quite linear. The fluidity-temperature curve for pure naphthalene, Fig. 4, can be safely extrapolated from 79.5°C down to 78°C for 100 rhes, where the association is found to be 1.254.

### Esters of oxalic acid

In Fig. 5 there is given the association of the esters of oxalic acid plotted against the number of carbon atoms in the ester. It is clear that the association of oxalic acid is very high but it is not possible to arrive at any definite value by this method. The value obtained later from the

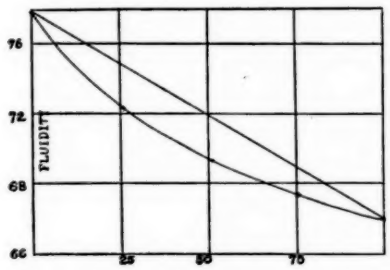


FIG. 1. The fluidities of mixtures of benzyl benzoate and benzoic acid at 120°C. Volume percent benzoic acid. Volume percent benzyl benzoate. Temperature 120°C.

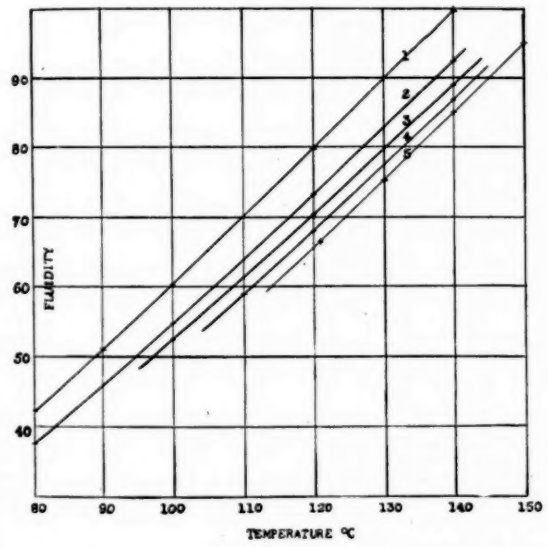


FIG. 2. Fluidity-temperature curves of mixtures of benzyl benzoate and benzoic acid. 1. Benzyl benzoate 100 percent; 2. Benzyl benzoate 75 percent, benzoic acid 25 percent; 3. Benzyl benzoate 50 percent, benzoic acid 50 percent; 4. Benzyl benzoate 25 percent, benzoic acid 75 percent; 5. Benzoic acid 100 percent.

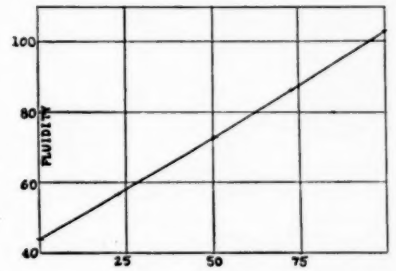


FIG. 3. The fluidities of mixtures of naphthalene and benzyl benzoate at 80°C.

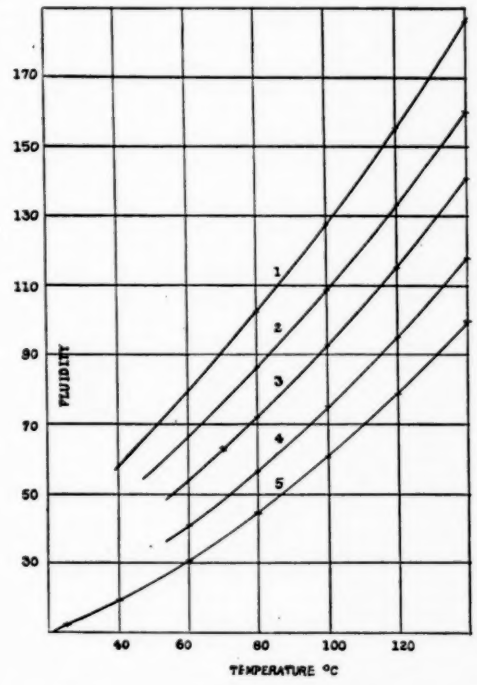


FIG. 4. The temperature-fluidity curves of mixtures of naphthalene and benzyl benzoate. 1. Naphthalene 100 percent; 2. Naphthalene 75 percent, benzyl benzoate 25 percent; 3. Naphthalene 50 percent, benzyl benzoate 50 percent; 4. Naphthalene 25 percent, benzyl benzoate 75 percent; 5. Benzyl benzoate 100 percent.

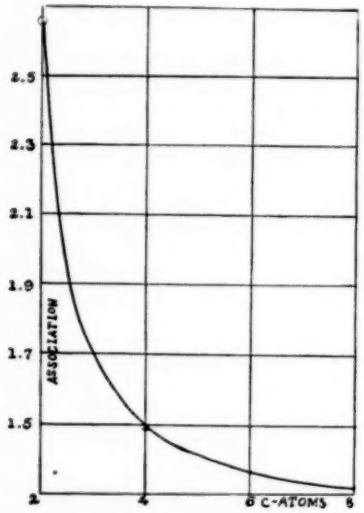


FIG. 5. The associations of esters of dibasic acids at a fluidity of 50 rhes. The value for oxalic acid obtained from Table II has been added to complete the curve. 2. Oxalic acid; 4. Dimethyl oxalate; 6. Diethyl oxalate; 8. *n*-dipropyl oxalate.

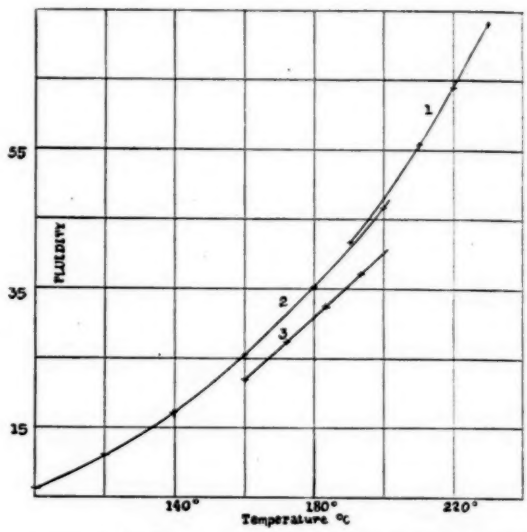


FIG. 6. The fluidity temperature curves of the dibasic acids. 1. Succinic acid. 2. Glutaric acid. 3. Adipic acid.

higher acids was inserted on this graph as an extrapolated value.

It is worthy of remark that dimethyl oxalate is less fluid than diethyl oxalate which is contrary to the behavior of all other esters studied. This merely indicates that the two methyl groups have only partly protected the oxalic acid so that the effective weight of the diethyl compound is less than that of the dimethyl compound, which is more highly associated.

### The higher acids

Going to the higher acids, Fig. 6, the temperature curves are in the normal order but succinic acid would cross the curve of glutaric acid somewhat below its melting point, 187°C, due to its higher association. It has often been noted that the highly associated compounds have the higher temperature coefficient of fluidity.

On plotting the associations of the acids, Fig. 7, it is found that they lie on a smooth curve which is nearly linear. From this curve it is possible to reach values for the association of both malonic acid, 2.46 at 50 rhes, and oxalic acid, 2.65 at 50 rhes. As seen in Fig. 5 the association of oxalic acid is not out of harmony with the association of the esters of oxalic acid, Fig. 4.

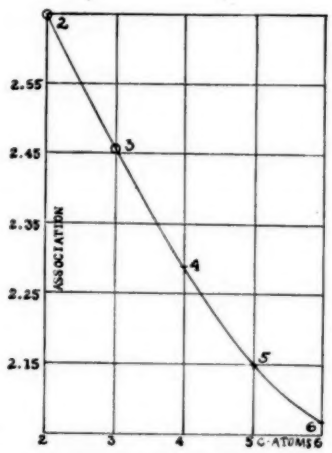


FIG. 7. The associations of the dibasic acids at a fluidity of 100 rhes. Points in circles are obtained by extrapolation. 2. Oxalic acid; 3. Malonic acid; 4. Succinic acid; 5. Glutaric acid; 6. Adipic acid.

Obviously it is theoretically possible to obtain these associations at more than one fluidity and thus calculate back in order to obtain several points on the fluidity temperature curve. The temperature centigrade for a fluidity of 50 rhes is found to be 123°C for oxalic acid and 131°C for malonic acid; succinic acid is 223°C.

# Some Viscosity Data for Boron Trioxide

GEORGE S. PARKS AND MONROE E. SPAGHT,[1] *Department of Chemistry, Stanford University*

(Received November 23, 1934)

The viscosities of four samples of pure molten boron trioxide have been measured between 267° and 443°C with a concentric cylinder viscometer. The results, representing true viscosity, range from $2.1\times10^{11}$ to $2.1\times10^{5}$ poises and are consistent with earlier data obtained at much higher temperatures. A viscosity value in the neighborhood of $10^{13}$ to $10^{14}$ poises appears to be associated with the so-called transition region in this and other glassy, or amorphous, materials.

## INTRODUCTION

FOR the studies on glass, which are now being carried on at Stanford University, boron trioxide has been selected as the typical inorganic material. It has the advantages of a very simple empirical formula, of easy preparation in a relatively pure condition, and of forming a glass which is remarkably stable toward devitrification. Previous investigations[2] have shown that the specific heats and the coefficients of thermal expansion of this glass, when it is heated, exhibit marked increases within a comparatively small range of temperature—principally between 225° and 250°C. Above this transition region the substance obviously becomes an extremely viscous liquid. The measurements presented here were made in order to provide some really quantitative viscosity data for boron trioxide in this viscous liquid state and to form a reliable estimate of the values which are attained within the "transition region" just mentioned.

## METHOD AND MATERIAL

The present study employed a concentric cylinder viscometer, which was essentially similar to that used by Parks, Barton, Spaght and Richardson[3] in their determinations of the viscosity of liquid glucose between 80° and 32°. A few modifications of this earlier apparatus were, of course, necessary in view of the higher temperatures involved in these measurements on boron trioxide. Thus the large, electrically-heated copper block which Thomas and Parks[2] developed for their specific heat measurements served as the adjustable thermostat. Into the cavity of this block was inserted a monel metal "outer cylinder" of the viscometer. This monel cylinder had an inside diameter of 2.5 cm and a depth of about 6 cm; by means of an external set-screw it could be locked tightly into place within the surrounding copper block. The inner viscometer cylinder, which rotated, was a monel rod, 0.63 cm in diameter and 23 cm long. It passed through a hole which had been bored through the center of the copper plug at the top of the cavity in the block and was held in proper position by two tool-steel bearings, mounted in this hole, in conjunction with a small adjustable steel collar. Temperatures were measured to $\pm0.05°$ by a White potentiometer and a platinum-platinrhodium thermocouple with one junction inserted into the copper block adjacent to the outer monel cylinder and the other junction at 0°C.

Other details and the general manipulation of the viscometer were the same as in the earlier study on liquid glucose.

The samples of boron trioxide used in this investigation were prepared from Merck's C. P. anhydrous $B_2O_3$ (impurities guaranteed to be less than 0.01 percent). This material was always heated in a platinum crucible for one to two hours at a temperature of about 1200°C in order to drive off the last traces of water and to eliminate gas bubbles. The molten oxide was then poured directly into the viscometer, which had been previously heated to the neighborhood of 500°.

[1] Shell Research Fellow for the scholastic year 1932–33.
[2] S. B. Thomas and G. S. Parks, J. Phys. Chem. **35**, 2091 (1931); M. E. Spaght and G. S. Parks, J. Phys. Chem. **38**, 103 (1934).
[3] G. S. Parks, L. E. Barton, M. E. Spaght and J. W. Richardson, Physics **5**, 193 (1934).

## The Viscosity Data

In the present study a total of thirty-two viscosity determinations were made between the temperatures of 267° and 443°C upon four different boron trioxide samples. The viscosities thus found varied from $2.1\times10^{11}$ to $2.06\times10^{5}$ poises. The values obtained with the different samples were highly concordant, as may be readily seen in Fig. 1 where the common logarithm of the viscosity has been plotted against the Centigrade temperatures.

Eight viscosity measurements between 750° and 1115°C have been made previously by Arndt,[4] using a falling body method. For purposes of completeness his results are also plotted in Fig. 1. It is obvious that a smooth curve may be drawn through both sets of experimental data.

In Table I we have recorded a series of "best values" corresponding to this smooth curve. Probably in all cases these represent true viscosity and not plasticity, as a number of tests carried out at various temperatures between 300° and 400° always gave us angular velocities of rotation which were directly proportional to the applied torque. One such test at 356.0°C is represented in Fig. 2, where the weight used in producing rotation of the inner cylinder of the viscometer has been varied tenfold; it is obvious that the resulting straight line passes through the origin.

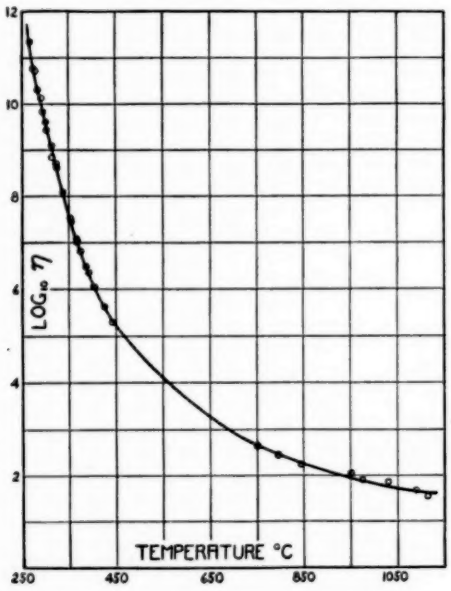


Fig. 1. A plot of the experimentally determined viscosity values for molten boron trioxide. The circles represent individual values; the heavy dots represent two or more values which practically coincide. The determinations below 450° are those of Parks and Spaght; those above 650° are those of Arndt.

[4] K. Arndt, Zeits. f. Elektrochemie **34**, 578 (1907).

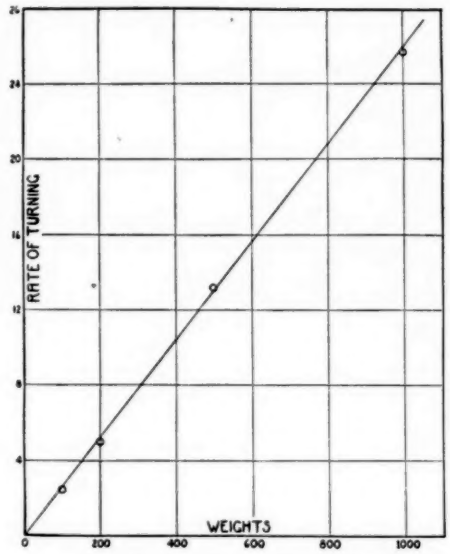


Fig. 2. A test of true viscosity at 356°. The *rate of turning* of the inner cylinder of the viscometer, in radians per second×1000, plotted against the *weight* used in producing the rotating torque.

Table I. *Viscosity data for boron trioxide.*

| T°C | Viscosity η (in poises) | $\text{Log}_{10}\,\eta$ | T°C | Viscosity η (in poises) | $\text{Log}_{10}\,\eta$ |
|---|---|---|---|---|---|
| 260 | $6.1\times10^{11}$ | 11.79 | 450 | $1.74\times10^{5}$ | 5.24 |
| 280 | $4.4\times10^{10}$ | 10.64 | 500 | $3.9\times10^{4}$ | 4.59 |
| 300 | $4.4\times10^{9}$ | 9.64 | 600 | $4.8\times10^{3}$ | 3.68 |
| 320 | $5.6\times10^{8}$ | 8.75 | 700 | $8.5\times10^{2}$ | 2.93 |
| 340 | $9.8\times10^{7}$ | 7.99 | 800 | $2.6\times10^{2}$ | 2.41 |
| 360 | $2.0\times10^{7}$ | 7.31 | 900 | $1.20\times10^{2}$ | 2.08 |
| 380 | $5.2\times10^{6}$ | 6.72 | 1000 | $7.4\times10$ | 1.87 |
| 400 | $1.62\times10^{6}$ | 6.21 | 1100 | $4.3\times10$ | 1.63 |

## Discussion

The transition region, within which such properties as the specific heat and coefficient of expansion change with unusual rapidity, centers around 240°C in the case of boron trioxide glass. While our actual viscosity measurements could not be carried conveniently below 267° with the

concentric cylinder viscometer, an extrapolation of the curve in Fig. 1 over an interval of merely 27°C is quite easy and reliable. From an enlargement of this figure we thus estimate $\eta = 10^{13.2}$ poises at 240°.

In the case of glucose glass the transition region centers around 25°C and the viscosity study[5] previously referred to yielded a value of $10^{13.1}$ poises at this temperature. A more recent, unpublished investigation in this laboratory also gives values ranging from $10^{13.2}$ to $10^{14.1}$ poises at 25°, depending on the extent of the annealing and previous working of some glassy glucose fibers. Moreover, some viscosity studies on commercial inorganic glasses[5] have yielded values in the neighborhood of $10^{13.7}$ poises for this transition region.

It thus appears that the *transition region* in glass-forming materials, whether these be inorganic or organic in character, or composed of only one component or of several components, can be in general identified with a viscosity of the order of $10^{13}$ to $10^{14}$ poises. This rule, while purely empirical at present, should be very useful in the study of amorphous solids.

[5] W. E. S. Turner, *The Constitution of Glass*, The Society of Glass Technology, Sheffield, England (1927), pp. 73 and 160. See also Samsoen, Comptes rendus **182**, 517 (1926).

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FEBRUARY, 1935 PHYSICS VOLUME 6

# The Viscosity of Mixtures of Liquids at High Pressures[1]

R. B. Dow, *Research Laboratory of Physics, Harvard University*

(Received December 10, 1934)

The effects of pressure and temperature change on the viscosity of organic, binary mixtures have been investigated by methods developed and used by P. W. Bridgman. Six mixtures have been examined over the entire concentration range at two temperatures, 30° and 75°C, and at pressures extending to 12,000 kg/cm². The isobaric, log viscosity-concentration curves for *n*-hexane carbon disulphide, and *n*-hexane *n*-decane are linear at both temperatures, indicating that these mixtures obey Arrhenius' empirical equation for the viscosity of a binary mixture. It is believed that a comparatively simple type of interlocking among molecules occurs in these mixtures due to the effectively linear structure of the molecules and the absence of non-uniform molecular fields such as would cause some sort of association. For the remaining mixtures: *n*-hexane diethyl ether, *n*-hexane chlorobenzene, *n*-pentane benzene, and eugenol carbon disulphide, the corresponding viscosity isobars are more complex; irregularities occur in certain regions of concentration which vary with temperature and pressure. In these latter mixtures, the interlocking at high pressures is complicated by the structural differences of the component molecules and their effects. The viscosity of *n*-decane as a function of pressure and temperature has also been investigated. Density data at atmospheric pressure and 30° are included in the paper.

TO study the effect of hydrostatic pressure on the viscosity of pure liquids, P. W. Bridgman[2] investigated forty-three pure liquids through a pressure range of 12,000 kg/cm² at 30° and 75°C. His data indicate that viscosity at high pressures is entirely different from that at ordinary conditions and that the "free-space" between molecules is largely decreased, crowding the molecules together in such a way that some sort of interlocking takes place. This conception gives a possible reason for the great increase in viscosity at high pressures.

It becomes interesting to extend such measurements of viscosity at high pressures to include mixtures of liquids for it is obvious that with different kinds of molecules in mixture the interlocking can be studied more completely than for pure liquids, since it is believed that the degree of interlocking depends on the size and shape of molecules. Consequently, this paper is devoted to the effects of various pressures and temperatures on the viscosity of six liquid, organic mixtures. With the exception of *n*-decane, the pure liquids used for the mixtures have been

[1] This paper is a summary of a thesis presented to the Graduate School of Arts and Sciences, Harvard University in partial fulfilment of the requirements for the Ph.D. in physics (1933).

[2] P. W. Bridgman, Proc. Am. Acad. **61**, 57 (1926).

studied by Bridgman.[2] The viscosity of *n*-decane at 30° and 75°C through a pressure range of 6000 kg/cm² is included in this investigation. In addition to the viscosity measurements, the density-concentration data at 30°C and atmospheric pressure are recorded for completeness.

## Method and Experimental Procedure

The method of preparing the mixtures was comparatively simple. The volume of each liquid was determined by a calibrated pipette which discharged between two graduations, and immediately after mixing, the density of the mixture at 30° was determined by a calibrated pycnometer which was fitted with ground glass caps to prevent evaporation.

The method employed in the viscosity measurements was that of Bridgman.[2] As the viscometer has been described previously,[2, 3, 4] it will suffice to recall the essentials of the instrument for the reader. It is of the falling-weight type consisting of a small cylindrical weight which is allowed to fall a few centimeters in a hollow steel cylinder of slightly larger internal diameter, the time of fall being measured electrically with a suitable timing device. In this way, the relative viscosity is measured by the time of fall. The time of fall could be found in opposite directions by enclosing the viscometer in a specially shaped pressure chamber which was connected to the remainder of the pressure apparatus in such a way that the whole assembly could be rotated through 180° by hand.

The pressure apparatus was of the type commonly used by Bridgman[3] in his investigations at high pressures, and was set up horizontally so that the viscometer could be rotated in a simple way. The pressures were determined as previously in this laboratory by measuring the changes of resistance of a manganin coil that was connected in the high pressure side of the press. The pressure chamber that contained the viscometer was surrounded by a constant temperature bath of water, the temperature being read on a corrected thermometer.

[3] P. W. Bridgman, *Physics of High Pressure*, Chap. 12, The Macmillan Co. (1931).
[4] E. Hatschek, *Viscosity of Liquids*, Chap. 6, Blackie and Sons (1928).

Table I. *Densities, ζ (in g/cm³) of mixtures of varying concentrations (in mole percent).*

| Conc. | Dens. | Conc. | Dens. | Conc. | Dens. | Conc. | Dens. |
|---|---|---|---|---|---|---|---|
| 1. *n*-HEXANE CARBON DISULPHIDE | | 2. *n*-HEXANE DIETHYL ETHER | | 4. *n*-HEXANE CHLORO-BENZENE | | 5. *n*-PENTANE BENZENE | |
| 31.8 | 0.959 | 0.0 | 0.701 | 49.0 | 0.851 | 43.8 | 0.748 |
| 58.2 | 0.802 | 33.1 | 0.682 | 75.5 | 0.975 | 11.5 | 0.837 |
| 41.1 | 0.890 | 28.3 | 0.685 | 34.0 | 0.787 | 66.2 | 0.693 |
| 20.2 | 1.043 | 35.4 | 0.679 | 63.0 | 0.914 | 82.4 | 0.657 |
| 13.4 | 1.110 | 41.8 | 0.673 | 100.0 | 1.098 | 28.0 | 0.787 |
| 4.9 | 1.190 | 79.8 | 0.662 | 88.4 | 1.042 | 52.3 | 0.725 |
| 0.0 | 1.244 | 49.7 | 0.673 | 17.6 | 0.722 | 75.1 | 0.672 |
| 82.9 | 0.702 | 16.5 | 0.692 | 94.6 | 1.074 | 100.0 | 0.617 |
| 46.4 | 0.856 | 75.5 | 0.662 | 5.1 | 0.678 | 0.0 | 0.869 |
| 41.1 | 0.890 | 84.1 | 0.659 | 1.8 | 0.667 | 59.2 | 0.707 |
| 73.5 | 0.738 | | | 97.3 | 1.087 | 36.2 | 0.765 |
| 65.1 | 0.771 | 3. *n*-HEXANE *n*-DECANE | | 90.0 | 1.050 | 19.8 | 0.809 |
| 54.7 | 0.816 | | | 69.6 | 0.945 | 55.6 | 0.716 |
| 100.0 | 0.654 | 40.1 | 0.687 | 87.4 | 1.036 | | |
| | | | | 92.8 | 1.062 | 6. EUGENOL CARBON DISULPHIDE | |
| 2. *n*-HEXANE DIETHYL ETHER | | 100.0 | 0.727 | 96.4 | 1.082 | | |
| | | 70.0 | 0.707 | | | 10.5 | 1.194 |
| | | 28.6 | 0.680 | 91.5 | 1.056 | 28.2 | 1.143 |
| 44.2 | 0.671 | 59.2 | 0.700 | 9.9 | 0.692 | 54.1 | 1.097 |
| 70.2 | 0.658 | 85.7 | 0.717 | 3.5 | 0.670 | 20.8 | 1.161 |
| 20.8 | 0.689 | 50.4 | 0.694 | 13.0 | 0.706 | 43.9 | 1.116 |
| 29.8 | 0.684 | 19.7 | 0.673 | 7.6 | 0.684 | 52.0 | 1.100 |
| 34.6 | 0.680 | 4.6 | 0.663 | 9.0 | 0.690 | 0.0 | 1,244 |
| 55.9 | 0.668 | 13.5 | 0.670 | 95.0 | 1.076 | 100.0 | 1.054 |
| 88.8 | 0.656 | 94.1 | 0.723 | 80.0 | 0.998 | 69.2 | 1.078 |
| 10.2 | 0.698 | 77.0 | 0.712 | 3.0 | 0.669 | 86.8 | 1.062 |
| 100.0 | 0.654 | 0.0 | 0.660 | 11.5 | 0.700 | 33.9 | 1.130 |
| | | | | 0.0 | 0.660 | 5.1 | 1.219 |
| | | | | | | 80.0 | 1.067 |

## Data

The following six mixtures were studied through the entire range of concentration: *n*-hexane carbon disulphide, *n*-hexane diethyl ether, *n*-hexane *n*-decane, *n*-hexane chlorobenzene, *n*-pentane benzene, and eugenol carbon disulphide. Most of the liquids were of the best grade of Eastman and some were further purified by redistilling. Table I is a summary of the density data obtained as results of the pycnometer measurements.

The measured quantities for a viscosity determination were time of fall, pressure and temperature. The viscosity was computed from the time of fall by applying correction formulas[2] for the various errors caused by pressure effects. Following Bridgman, the common logarithm of the viscosity, instead of the viscosity itself, is given because of the very rapid increase of viscosity with increase of pressure. The viscosity of each mixture at atmospheric pressure at 30° was taken as unity, and the relative viscosity computed from $\log_{10} t/t_0$, $t$ being the corrected time of fall at a certain pressure and temperature, and $t_0$ the time of fall at atmospheric pressure at 30°. The values of $\log_{10} t/t_0$ at 30° and 75°,

TABLE II. *Viscosity of n-decane.* Values of $\log t/t_0$ where $t_0$ is the time of fall at 30°C and atmospheric pressure ($\log t_0 = 0.826$).

| Pressure (kg/cm²) | Log $t/t_0$ 30° | 75° |
|---|---|---|
| 1 | 0.000 | 0.208 |
| 500 | 0.184 | 0.005 |
| 1000 | 0.356 | |
| 2000 | 0.659 | 0.359 |
| 3000 | 0.939 | 0.585 |
| 4000 | 1.212 | 0.785 |
| 6000 | | 1.163 |

$\log_{10} t_0$,[5] and the pressures in kg/cm² are given in Table II for *n*-decane, and with the molar concentrations in Table III for the six binary mixtures. In the course of these experiments, the viscosities of the pure liquids were redetermined and the values found to be in good agreement with those of Bridgman, the disagreement in any case not amounting to over two percent.

As Table III does not show the interesting and unusual features exhibited by these results, isobaric viscosity-concentration diagrams are given in several instances in order that the significance of the data may be better visualized.

It is difficult to estimate the error in these experiments. The total percentage error estimated for a typical mixture of *n*-hexane chlorobenzene at a pressure of 500 kg/cm² at 30° amounted to about two percent, and increased to three percent at 75°. At higher pressures these errors became less. However, on estimating that part of the error contributed by the data of Table III by considering how well the experimental points fitted a smooth curve, the maximum deviation of a plotted point from the smooth viscosity-pressure curve for the same mixture at 30° corresponded to an error of 0.5 percent in the fall time. The remaining 7 points fitted the curve within the error of drawing. The similar curve at 75° showed that all the points fitted it without any noticeable deviations. Consequently, since the greater part of the total error came from the errors in the quantities of Table III, it is reasonable to expect that the total error amounted to less than that estimated as the percentage error.

[5] The viscometer was not designed for high accuracy in the time of fall, $t_0$ at atmospheric pressure; hence these values should be used with caution in further applications.

## DISCUSSION OF RESULTS

### (1) Viscosity of *n*-decane at various pressures and temperatures

The viscosity of *n*-pentane, *n*-hexane and *n*-octane of the methane series has been investigated under various pressure and temperature conditions by Bridgman.[2] The data of this paper extend these measurements to include *n*-decane. In general, the pressure coefficient of viscosity, as well as the temperature coefficient, is similar to those of the other paraffins that have been studied. The relation between the logarithm of viscosity and molecular weight is apparently simple for the members of this series at high pressures. By plotting log viscosity against molecular weight for these liquids at 4000 kg/cm² and 30°, it will be found that the points lie on a curve which closely approaches a straight line. Also, at 75° a similar curve at 6000 kg/cm² approaches linearity.

### (2) Viscosity-concentration curves at constant pressure, at 30° and 75°

The isobaric viscosity-concentration curves, plotted from the data of Table III, may be conveniently divided into two classes. First, the curves for which the log relative viscosity is a linear function of the molar concentration through the entire pressure range at 30° and 75°, representing the mixtures *n*-hexane carbon disulphide and *n*-hexane *n*-decane, Figs. 1 and 2, the curves at 75° being omitted as they are qualitatively similar. Secondly, the curves of the remaining mixtures under similar conditions for which the log relative viscosity varies in a complicated way with the molar concentration, Figs. 3 to 9 inclusive.

The components of the mixtures of the first group are similar in that they are simple nonpolar liquids which would be expected to dissolve in solution without the complications due to nonuniform molecular fields. *A priori*, it might be thought that the tendency of the molecules would be toward an end-to-end arrangement, contributing to an orientation more or less parallel to the lines of flow, the viscosity being the resistance of these parallel layers of molecules

TABLE III. *Viscosity of mixtures as function of concentration and pressure.*

| Pressure (kg/cm²) | Log $t/t_0$ 30° | 75° | Log $t/t_0$ 30° | 75° |
|---|---|---|---|---|
| **1. *n*-HEXANE CARBON DISULPHIDE** | | | | |
| | 31.8 mole % $C_6H_{14}$ log $t_0$ = 0.508 | | 58.2 mole % $C_6H_{14}$ log $t_0$ = 0.470 | |
| 1 | 0.000 | 0.103 | 0.000 | 0.153 |
| 500 | 0.104 | 0.003 | 0.150 | 0.015 |
| 1000 | 0.202 | 0.089 | 0.259 | 0.102 |
| 2000 | 0.371 | 0.242 | 0.447 | 0.297 |
| 4000 | 0.644 | 0.471 | 0.750 | 0.570 |
| 6000 | 0.849 | 0.660 | 0.990 | 0.785 |
| 8000 | 1.031 | 0.830 | 1.226 | 0.965 |
| 10000 | 1.239 | 1.015 | 1.480 | 1.169 |
| | 13.4 mole % $C_6H_{14}$ log $t_0$ = 0.529 | | 4.9 mole % $C_6H_{14}$ log $t_0$ = 0.537 | |
| 1 | 0.000 | 0.141 | 0.000 | 0.117 |
| 500 | 0.093 | 0.041 | 0.080 | 0.040 |
| 1000 | 0.165 | 0.050 | 0.159 | 0.031 |
| 2000 | 0.339 | 0.201 | 0.304 | 0.159 |
| 4000 | 0.574 | 0.444 | 0.540 | 0.364 |
| 6000 | 0.740 | 0.633 | 0.707 | 0.528 |
| 8000 | 0.902 | 0.749 | 0.880 | 0.669 |
| 10000 | 1.109 | 0.900 | 1.060 | 0.831 |
| | 20.2 mole % $C_6H_{14}$ log $t_0$ = 0.498 | | 46.4 mole % $C_6H_{14}$ log $t_0$ = 0.470 | |
| 1 | 0.000 | 0.117 | 0.000 | 0.124 |
| 500 | 0.100 | 0.024 | 0.136 | 0.005 |
| 1000 | 0.195 | 0.060 | 0.230 | 0.100 |
| 2000 | 0.349 | 0.106 | 0.425 | 0.276 |
| 4000 | 0.599 | 0.427 | 0.695 | 0.533 |
| 6000 | 0.791 | 0.618 | 0.918 | 0.732 |
| 8000 | 0.979 | 0.789 | 1.140 | 0.891 |
| 10000 | 1.201 | 0.831 | 1.390 | 1.076 |
| | 41.1 mole % $C_6H_{14}$ log $t_0$ = 0.484 | | 82.9 mole % $C_6H_{14}$ log $t_0$ = 0.452 | |
| 1 | 0.000 | 0.132 | 0.000 | 0.111 |
| 500 | 0.126 | 0.024 | 0.164 | 0.012 |
| 1000 | 0.226 | 0.075 | 0.295 | 0.125 |
| 2000 | 0.407 | 0.247 | 0.520 | 0.325 |
| 4000 | 0.669 | 0.499 | 0.850 | 0.640 |
| 6000 | 0.900 | 0.705 | 1.130 | 0.885 |
| 8000 | 1.100 | 0.886 | 1.398 | 1.092 |
| 10000 | 1.332 | 1.057 | 1.665 | 1.310 |
| | 73.5 mole % $C_6H_{14}$ log $t_0$ = 0.440 | | 54.7 mole % $C_6H_{14}$ log $t_0$ = 0.465 | |
| 1 | 0.000 | 0.158 | 0.000 | 0.119 |
| 500 | 0.151 | 0.000 | 0.125 | 0.008 |
| 1000 | 0.279 | 0.128 | 0.240 | 0.097 |
| 2000 | 0.492 | 0.330 | 0.440 | 0.282 |
| 4000 | 0.820 | 0.610 | 0.740 | 0.560 |
| 6000 | 1.080 | 0.828 | 0.966 | 0.775 |
| 8000 | 1.326 | 1.035 | 1.198 | 0.940 |
| 10000 | 1.606 | 1.258 | 1.469 | 1.140 |
| | 65.1 mole % $C_6H_{14}$ log $t_0$ = 0.455 | | | |
| 1 | 0.000 | 0.133 | | |
| 500 | 0.160 | 0.002 | | |
| 1000 | 0.239 | 0.115 | | |
| 2000 | 0.470 | 0.310 | | |
| 4000 | 0.765 | 0.590 | | |
| 6000 | 1.036 | 0.805 | | |
| 8000 | 1.290 | 1.000 | | |
| 10000 | 1.520 | 1.220 | | |
| **2. *n*-HEXANE DIETHYL ETHER** | | | | |
| | 44.2 mole % $C_6H_{14}$ log $t_0$ = 0.362 | | 70.2 mole % $C_6H_{14}$ log $t_0$ = 0.398 | |
| 1 | 0.000 | 0.054 | 0.000 | 0.113 |
| 500 | 0.131 | 0.041 | 0.139 | 0.010 |
| 1000 | 0.253 | 0.130 | 0.260 | 0.122 |
| 2000 | 0.470 | 0.299 | 0.470 | 0.319 |
| 4000 | 0.813 | 0.600 | 0.795 | 0.632 |
| 6000 | 1.089 | 0.860 | 1.089 | 0.881 |
| 8000 | 1.341 | 1.090 | 1.379 | 1.091 |
| 10000 | 1.617 | 1.281 | 1.677 | 1.290 |
| 12000 | | 1.490 | | 1.490 |

| Pressure (kg/cm²) | Log $t/t_0$ 30° | 75° | Log $t/t_0$ 30° | 75° |
|---|---|---|---|---|
| **2. *n*-HEXANE DIETHYL ETHER—*Continued.*** | | | | |
| | 20.8 mole % $C_6H_{14}$ log $t_0$ = 0.352 | | 29.8 mole % $C_6H_{14}$ log $t_0$ = 0.359 | |
| 1 | 0.000 | 0.080 | 0.000 | 0.060 |
| 500 | 0.134 | 0.036 | 0.118 | 0.032 |
| 1000 | 0.248 | 0.141 | 0.225 | 0.120 |
| 2000 | 0.442 | 0.323 | 0.414 | 0.280 |
| 4000 | 0.739 | 0.606 | 0.721 | 0.549 |
| 6000 | 0.972 | 0.822 | 0.997 | 0.769 |
| 8000 | 1.210 | 1.000 | 1.239 | 0.959 |
| 10000 | 1.447 | 1.164 | 1.475 | 1.143 |
| 12000 | | 1.315 | | 1.330 |
| | 34.6 mole % $C_6H_{14}$ log $t_0$ = 0.348 | | 55.9 mole % $C_6H_{14}$ log $t_0$ = 0.371 | |
| 1 | 0.000 | 0.005 | 0.000 | 0.110 |
| 500 | 0.132 | 0.079 | 0.148 | 0.005 |
| 1000 | 0.250 | 0.160 | 0.273 | 0.111 |
| 2000 | 0.450 | 0.311 | 0.485 | 0.304 |
| 4000 | 0.752 | 0.572 | 0.809 | 0.609 |
| 6000 | 1.012 | 0.809 | 1.095 | 0.842 |
| 8000 | 1.272 | 1.015 | 1.364 | 1.049 |
| 10000 | 1.529 | 1.202 | 1.619 | 1.261 |
| 12000 | | 1.380 | | 1.469 |
| | 88.8 mole % $C_6H_{14}$ log $t_0$ = 0.401 | | 10.2 mole % $C_6H_{14}$ log $t_0$ = 0.324 | |
| 1 | 0.000 | 0.109 | 0.000 | 0.044 |
| 500 | 0.143 | 0.022 | 0.130 | 0.040 |
| 1000 | 0.275 | 0.139 | 0.241 | 0.121 |
| 2000 | 0.501 | 0.342 | 0.431 | 0.270 |
| 4000 | 0.857 | 0.639 | 0.729 | 0.526 |
| 6000 | 1.165 | 0.883 | 0.979 | 0.743 |
| 8000 | 1.474 | 1.109 | 1.210 | 0.942 |
| 10000 | 1.770 | 1.330 | 1.428 | 1.130 |
| 12000 | | 1.550 | | 1.314 |
| | 33.1 mole % $C_6H_{14}$ log $t_0$ = 0.349 | | 28.3 mole % $C_6H_{14}$ log $t_0$ = 0.346 | |
| 1 | 0.000 | 0.094 | 0.000 | 0.095 |
| 500 | 0.140 | 0.022 | 0.141 | 0.019 |
| 1000 | 0.262 | 0.129 | 0.262 | 0.121 |
| 2000 | 0.469 | 0.310 | 0.456 | 0.305 |
| 4000 | 0.790 | 0.596 | 0.739 | 0.591 |
| 6000 | 1.057 | 0.825 | 0.994 | 0.812 |
| 8000 | 1.306 | 1.028 | 1.250 | 1.009 |
| 10000 | 1.540 | 1.204 | 1.506 | 1.199 |
| 12000 | | 1.395 | | 1.389 |
| | 35.4 mole % $C_6H_{14}$ log $t_0$ = 0.361 | | 41.8 mole % $C_6H_{14}$ log $t_0$ = 0.354 | |
| 1 | 0.000 | 0.110 | 0.000 | 0.090 |
| 500 | 0.129 | 0.009 | 0.133 | 0.012 |
| 1000 | 0.247 | 0.120 | 0.253 | 0.110 |
| 2000 | 0.450 | 0.313 | 0.456 | 0.295 |
| 4000 | 0.771 | 0.605 | 0.764 | 0.601 |
| 6000 | 1.049 | 0.830 | 1.055 | 0.860 |
| 8000 | 1.320 | 1.039 | 1.340 | 1.089 |
| 10000 | 1.601 | 1.244 | 1.629 | 1.300 |
| 12000 | | 1.450 | | 1.491 |
| **3. *n*-HEXANE *n*-DECANE** | | | | |
| | 40.1 mole % $C_{10}H_{22}$ log $t_0$ = 0.580 | | 70.0 mole % $C_{10}H_{22}$ log $t_0$ = 0.716 | |
| 1 | 0.000 | 0.175 | 0.000 | 0.194 |
| 500 | 0.185 | 0.016 | 0.186 | 0.002 |
| 1000 | 0.342 | 0.136 | 0.347 | 0.098 |
| 2000 | 0.600 | 0.382 | 0.633 | 0.347 |
| 3000 | 0.810 | 0.554 | 0.878 | 0.561 |
| 4000 | 1.021 | 0.757 | 1.125 | 0.765 |
| | 28.6 mole % $C_{10}H_{22}$ log $t_0$ = 0.520 | | 59.2 mole % $C_{10}H_{22}$ log $t_0$ = 0.657 | |
| 1 | 0.000 | 0.159 | 0.000 | 0.166 |
| 500 | 0.179 | 0.001 | 0.187 | 0.013 |
| 1000 | 0.331 | 0.136 | 0.349 | 0.135 |
| 2000 | 0.580 | 0.355 | 0.620 | 0.373 |
| 3000 | 0.795 | 0.549 | 0.856 | 0.580 |
| 4000 | 0.992 | 0.727 | 1.089 | 0.767 |

| Pressure (kg/cm²) | Log $t/t_0$ 30° | 75° | Log $t/t_0$ 30° | 75° |
|---|---|---|---|---|
| **3. *n*-HEXANE *n*-DECANE—*Continued.*** | | | | |
| | 85.7 mole % $C_{10}H_{22}$ log $t_0$ = 0.768 | | 50.4 mole % $C_{10}H_{22}$ log $t_0$ = 0.631 | |
| 1 | 0.000 | 0.196 | 0.000 | 0.186 |
| 500 | 0.199 | 0.016 | 0.187 | 0.010 |
| 1000 | 0.362 | 0.110 | 0.350 | 0.120 |
| 2000 | 0.642 | 0.367 | 0.620 | 0.379 |
| 3000 | 0.909 | 0.585 | 0.841 | 0.564 |
| 4000 | 1.170 | 0.783 | 1.061 | 0.758 |
| | 19.7 mole % $C_{10}H_{22}$ log $t_0$ = 0.503 | | 4.6 mole % $C_{10}H_{22}$ log $t_0$ = 0.420 | |
| 1 | 0.000 | 0.151 | 0.000 | 0.135 |
| 500 | 0.175 | 0.010 | 0.179 | 0.012 |
| 1000 | 0.328 | 0.163 | 0.327 | 0.140 |
| 2000 | 0.581 | 0.363 | 0.563 | 0.360 |
| 3000 | 0.791 | 0.549 | 0.749 | 0.539 |
| 4000 | 0.970 | 0.712 | 0.926 | 0.705 |
| | 13.5 mole % $C_{10}H_{22}$ log $t_0$ = 0.462 | | 94.1 mole % $C_{10}H_{22}$ log $t_0$ = 0.801 | |
| 1 | 0.000 | 0.137 | 0.000 | 0.231 |
| 500 | 0.187 | 0.017 | 0.179 | 0.006 |
| 1000 | 0.336 | 0.157 | 0.347 | 0.103 |
| 2000 | 0.570 | 0.377 | 0.650 | 0.374 |
| 3000 | 0.769 | 0.557 | 0.921 | 0.597 |
| 4000 | 0.954 | 0.710 | 1.198 | 0.781 |
| | 77.0 mole % $C_{10}H_{22}$ log $t_0$ = 0.731 | | | |
| 1 | 0.000 | 0.204 | | |
| 500 | 0.181 | 0.004 | | |
| 1000 | 0.340 | 0.115 | | |
| 2000 | 0.629 | 0.364 | | |
| 3000 | 0.876 | 0.574 | | |
| 4000 | 1.112 | 0.767 | | |
| **4. *n*-HEXANE CHLOROBENZENE** | | | | |
| | 49.0 mole % $C_6H_5Cl$ log $t_0$ = 0.563 | | 75.5 mole % $C_6H_5Cl$ log $t_0$ = 0.681 | |
| 1 | 0.000 | 0.160 | 0.000 | 0.186 |
| 500 | 0.122 | 0.040 | 0.131 | 0.067 |
| 1000 | 0.242 | 0.075 | 0.253 | 0.047 |
| 2000 | 0.466 | 0.290 | 0.476 | 0.251 |
| 4000 | 0.860 | 0.639 | 0.860 | 0.585 |
| 6000 | 1.212 | 0.921 | 1.277 | 0.861 |
| 8000 | 1.530 | 1.150 | 1.778 | 1.147 |
| | 34.0 mole % $C_6H_5Cl$ log $t_0$ = 0.509 | | 63.0 mole % $C_6H_5Cl$ log $t_0$ = 0.628 | |
| 1 | 0.000 | 0.145 | 0.000 | 0.169 |
| 500 | 0.136 | 0.010 | 0.127 | 0.044 |
| 1000 | 0.260 | 0.109 | 0.249 | 0.072 |
| 2000 | 0.476 | 0.308 | 0.460 | 0.272 |
| 4000 | 0.820 | 0.600 | 0.840 | 0.586 |
| 6000 | 1.137 | 0.847 | 1.210 | 0.831 |
| 8000 | 1.505 | 1.132 | 1.590 | 1.104 |
| | 88.4 mole % $C_6H_5Cl$ log $t_0$ = 0.749 | | 17.6 mole % $C_6H_5Cl$ log $t_0$ = 0.463 | |
| 1 | 0.000 | 9.815 | 0.000 | 0.174 |
| 500 | 0.117 | 9.932 | 0.115 | 0.026 |
| 1000 | 0.234 | 0.040 | 0.230 | 0.101 |
| 2000 | 0.462 | 0.234 | 0.450 | 0.309 |
| 4000 | 0.900 | 0.555 | 0.864 | 0.608 |
| 6000 | 1.330 | 0.842 | 1.257 | 0.850 |
| 8000 | 1.760 | 1.170 | 1.630 | 1.095 |
| | 94.6 mole % $C_6H_5Cl$ log $t_0$ = 0.766 | | 5.1 mole % $C_6H_5Cl$ log $t_0$ = 0.419 | |
| 1 | 0.000 | 9.810 | 0.000 | 0.155 |
| 500 | 0.115 | 9.939 | 0.141 | 0.010 |
| 1000 | 0.225 | 0.025 | 0.276 | 0.115 |
| 2000 | 0.439 | 0.214 | 0.529 | 0.325 |
| 4000 | 0.892 | 0.521 | 0.960 | 0.639 |
| 6000 | 1.403 | 0.809 | 1.316 | 0.881 |
| 7000 | 1.701 | | | |
| 8000 | | 1.156 | 1.965 | 1.144 |

4. *n*-HEXANE CHLOROBENZENE—*Continued.*

| Pressure (kg/cm²) | Log $t/t_0$ 30° | 75° | Log $t/t_0$ 30° | 75° |
|---|---|---|---|---|
| | 1.8 mole % $C_6H_5Cl$ log $t_0$ = 0.405 | | 97.3 mole % $C_6H_5Cl$ log $t_0$ = 0.773 | |
| 1 | 0.000 | 0.124 | 0.000 | 0.175 |
| 500 | 0.163 | 0.015 | 0.124 | 0.063 |
| 1000 | 0.304 | 0.135 | 0.241 | 0.043 |
| 2000 | 0.547 | 0.338 | 0.460 | 0.233 |
| 4000 | 0.927 | 0.607 | 0.847 | 0.545 |
| 6000 | 1.219 | 0.895 | 1.170 | 0.840 |
| 8000 | 1.504 | 1.160 | | 1.180 |
| | 90.0 mcle % $C_6H_5Cl$ log $t_0$ = 0.765 | | 69.6 mole % $C_6H_5Cl$ log $t_0$ = 0.664 | |
| 1 | 0.000 | 0.217 | 0.000 | 0.165 |
| 500 | 0.116 | 0.095 | 0.135 | 0.043 |
| 1000 | 0.227 | 0.017 | 0.262 | 0.072 |
| 2000 | 0.440 | 0.215 | 0.496 | 0.266 |
| 4000 | 0.830 | 0.529 | 0.902 | 0.565 |
| 6000 | 1.226 | 0.812 | 1.260 | 0.830 |
| 8000 | | 1.140 | | 1.139 |
| | 87.4 mole % $C_6H_5Cl$ log $t_0$ = 0.730 | | 92.8 mole % $C_6H_5Cl$ log $t_0$ = 0.756 | |
| 1 | 0.000 | 0.180 | 0.000 | 0.179 |
| 500 | 0.115 | 0.060 | 0.114 | 0.069 |
| 1000 | 0.222 | 0.049 | 0.225 | 0.033 |
| 2000 | 0.421 | 0.231 | 0.441 | 0.221 |
| 4000 | 0.797 | 0.504 | 0.872 | 0.528 |
| 6000 | 1.179 | 0.787 | 1.372 | 0.828 |
| 8000 | | 1.120 | | 1.160 |
| | 96.4 mole % $C_6H_5Cl$ log $t_0$ = 0.788 | | 91.5 mole % $C_6H_5Cl$ log $t_0$ = 0.745 | |
| 1 | 0.000 | 0.190 | 0.000 | 0.175 |
| 500 | 0.113 | 0.078 | 0.112 | 0.056 |
| 1000 | 0.223 | 0.025 | 0.220 | 0.054 |
| 2000 | 0.430 | 0.212 | 0.427 | 0.245 |
| 4000 | 0.798 | 0.515 | 0.854 | 0.540 |
| 6000 | 1.123 | 0.820 | 1.322 | 0.839 |
| 8000 | | 1.192 | | 1.191 |
| | 9.9 mole % $C_6H_5Cl$ log $t_0$ = 0.433 | | 3.5 mole % $C_6H_5Cl$ log $t_0$ = 0.423 | |
| 1 | 0.000 | 0.143 | 0.000 | 0.150 |
| 500 | 0.160 | 0.006 | 0.155 | 0.002 |
| 1000 | 0.310 | 0.135 | 0.304 | 0.130 |
| 2000 | 0.586 | 0.350 | 0.581 | 0.336 |
| 4000 | 1.160 | 0.658 | 1.060 | 0.634 |
| 6000 | 1.552 | 0.882 | 1.492 | 0.878 |
| 8000 | | 1.177 | | 1.165 |
| | 13.0 mole % $C_6H_5Cl$ log $t_0$ = 0.435 | | 7.6 mole % $C_6H_5Cl$ log $t_0$ = 0.424 | |
| 1 | 0.000 | 0.120 | 0.000 | 0.155 |
| 500 | 0.136 | 0.004 | 0.136 | 0.002 |
| 1000 | 0.270 | 0.105 | 0.272 | 0.125 |
| 2000 | 0.510 | 0.294 | 0.505 | 0.331 |
| 4000 | 0.915 | 0.605 | 0.914 | 0.640 |
| 6000 | 1.298 | 0.831 | 1.284 | 0.851 |
| 8000 | 1.741 | 1.075 | 1.640 | 1.089 |
| | 9.0 mole % $C_6H_5Cl$ log $t_0$ = 0.428 | | 95.0 mcle % $C_6H_5Cl$ log $t_0$ = 0.770 | |
| 1 | 0.000 | 0.149 | 0.000 | 0.189 |
| 500 | 0.146 | 0.001 | 0.115 | 0.081 |
| 1000 | 0.286 | 0.127 | 0.226 | 0.021 |
| 2000 | 0.547 | 0.340 | 0.445 | 0.209 |
| 4000 | 0.997 | 0.650 | 0.855 | 0.519 |
| 6000 | 1.416 | 0.872 | 1.297 | 0.810 |
| 8000 | 1.880 | 1.130 | | 1.160 |
| | 80.0 mole % $C_6H_5Cl$ log $t_0$ = 0.700 | | 3.0 mole % $C_6H_5Cl$ log $t_0$ = 0.425 | |
| 1 | 0.000 | 0.190 | 0.000 | 0.145 |
| 500 | 0.120 | 0.075 | 0.159 | 0.003 |
| 1000 | 0.240 | 0.035 | 0.305 | 0.125 |
| 2000 | 0.470 | 0.235 | 0.566 | 0.331 |
| 4000 | 0.888 | 0.563 | 1.004 | 0.635 |
| 6000 | 1.319 | 0.841 | 1.414 | 0.887 |
| 8000 | | 1.162 | | 1.160 |

4. *n*-HEXANE CHLOROBENZENE—*Continued.*

| Pressure (kg/cm²) | Log $t/t_0$ 30° | 75° | Log $t/t_0$ 30° | 75° |
|---|---|---|---|---|
| | 11.5 mole % $C_6H_5Cl$ log $t_0$ = 0.440 | | | |
| 1 | 0.000 | 0.130 | | |
| 500 | 0.146 | 0.003 | | |
| 1000 | 0.284 | 0.124 | | |
| 2000 | 0.540 | 0.330 | | |
| 4000 | 0.981 | 0.630 | | |
| 6000 | 1.391 | 0.865 | | |
| 8000 | | 1.115 | | |

5. *n*-PENTANE BENZENE

| | | | | |
|---|---|---|---|---|
| | 43.8 mole % $C_5H_{12}$ log $t_0$ = 0.530 | | 11.5 mole % $C_5H_{12}$ log $t_0$ = 0.676 | |
| 1 | 0.000 | 0.130 | 0.000 | 0.153 |
| 500 | 0.115 | 0.010 | 0.139 | 0.037 |
| 1000 | 0.236 | 0.097 | 0.271 | 0.074 |
| 1500 | 0.363 | 0.195 | 0.399 | 0.181 |
| 2000 | 0.494 | 0.282 | 0.519 | 0.282 |
| 3000 | | 0.446 | | 0.471 |
| 4000 | | 0.590 | | 0.645 |
| | 66.2 mole % $C_5H_{12}$ log $t_0$ = 0.444 | | 82.4 mole % $C_5H_{12}$ log $t_0$ = 0.375 | |
| 1 | 0.000 | 0.120 | 0.000 | 0.132 |
| 500 | 0.125 | 0.002 | 0.138 | 0.002 |
| 1000 | 0.243 | 0.108 | 0.257 | 0.115 |
| 1500 | 0.355 | 0.206 | 0.362 | 0.214 |
| 2000 | 0.460 | 0.292 | 0.455 | 0.302 |
| 3000 | 0.656 | 0.446 | 0.614 | 0.454 |
| 4000 | | 0.576 | | 0.581 |
| | 28.0 mole % $C_5H_{12}$ log $t_0$ = 0.600 | | 52.3 mole % $C_5H_{12}$ log $t_0$ = 0.500 | |
| 1 | 0.000 | 0.131 | 0.000 | 0.119 |
| 500 | 0.130 | 0.054 | 0.120 | 0.003 |
| 1000 | 0.260 | 0.080 | 0.236 | 0.116 |
| 1500 | 0.384 | 0.179 | 0.347 | 0.220 |
| 2000 | 0.503 | 0.274 | 0.449 | 0.314 |
| 3000 | | 0.445 | | 0.479 |
| 4000 | | | | 0.625 |
| | 75.1 mole % $C_5H_{12}$ log $t_0$ = 0.405 | | 59.2 mole % $C_5H_{12}$ log $t_0$ = 0.475 | |
| 1 | 0.000 | 0.130 | 0.000 | 0.115 |
| 500 | 0.134 | 0.003 | 0.128 | 0.004 |
| 1000 | 0.254 | 0.110 | 0.247 | 0.100 |
| 1500 | 0.359 | 0.212 | 0.359 | 0.195 |
| 2000 | 0.453 | 0.302 | 0.454 | 0.284 |
| 3000 | | 0.455 | 0.626 | 0.440 |
| 4000 | | 0.590 | | 0.580 |
| | 36.2 mole % $C_5H_{12}$ log $t_0$ = 0.565 | | 19.8 mole % $C_5H_{12}$ log $t_0$ = 0.642 | |
| 1 | 0.000 | 0.136 | 0.000 | 0.175 |
| 500 | 0.133 | 0.004 | 0.127 | 0.051 |
| 1000 | 0.254 | 0.119 | 0.250 | 0.064 |
| 1500 | 0.362 | 0.227 | 0.367 | 0.169 |
| 2000 | 0.470 | 0.325 | 0.480 | 0.267 |
| 3000 | 0.668 | 0.500 | 0.689 | 0.442 |
| 4000 | | 0.704 | | |
| | 92.5 mole % $C_5H_{12}$ log $t_0$ = 0.339 | | 5.0 mole % $C_5H_{12}$ log $t_0$ = 0.710 | |
| 1 | 0.000 | 0.150 | 0.000 | 0.181 |
| 500 | 0.157 | 0.016 | 0.148 | 0.046 |
| 1000 | 0.296 | 0.146 | 0.290 | 0.078 |
| 1500 | 0.423 | 0.249 | 0.424 | 0.188 |
| 2000 | 0.537 | 0.332 | 0.550 | 0.290 |
| 3000 | 0.755 | 0.467 | | 0.463 |
| 4000 | | 0.567 | | |
| | 74.5 mole % $C_5H_{12}$ log $t_0$ = 0.407 | | | |
| 1 | 0.000 | 0.120 | | |
| 500 | 0.126 | 0.001 | | |
| 1000 | 0.251 | 0.110 | | |
| 1500 | 0.369 | 0.209 | | |
| 2000 | 0.476 | 0.290 | | |
| 3000 | 0.671 | 0.301 | | |

6. EUGENOL CARBON DISULPHIDE[6]

| Pressure (kg/cm²) | Log $t/t_0$ 30° | 75° | Log $t/t_0$ 30° | 75° |
|---|---|---|---|---|
| | 28.2 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.418 | | 76.0 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.429 | |
| 1 | 0.000 | 0.188 | 0.000 | 0.400 |
| 500 | 0.115 | 0.096 | 0.179 | 0.281 |
| 1000 | 0.223 | 0.007 | 0.357 | 0.159 |
| 2000 | 0.429 | 0.169 | 0.740 | 0.090 |
| 4000 | 0.819 | 0.490 | 1.572 | 0.611 |
| 6000 | 1.195 | 0.769 | 2.470 | 1.176 |
| 8000 | | 1.011 | | 1.828 |
| | 10.1 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.650 | | 20.7 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.770 | |
| 1 | 0.000 | 0.128 | 0.000 | 0.170 |
| 500 | 0.079 | 0.048 | 0.095 | 0.066 |
| 1000 | 0.157 | 0.026 | 0.184 | 0.030 |
| 2000 | 0.307 | 0.161 | 0.359 | 0.200 |
| 4000 | 0.581 | 0.385 | 0.720 | 0.461 |
| 6000 | 0.817 | 0.583 | 1.112 | 0.653 |
| 8000 | | 0.752 | | 0.799 |
| | 48.5 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.715 | | 39.6 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.382 | |
| 1 | 0.000 | 0.300 | 0.000 | 0.190 |
| 500 | 0.149 | 0.175 | 0.109 | 0.121 |
| 1000 | 0.293 | 0.053 | 0.216 | 0.051 |
| 2000 | 0.597 | 0.120 | 0.442 | 0.100 |
| 4000 | 1.213 | 0.579 | 0.996 | 0.420 |
| 6000 | 1.975 | 1.011 | 1.419 | 0.782 |
| 8000 | | 1.480 | | 1.210 |
| | 94.0 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.653 | | 5.1 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.155 | |
| 1 | 0.000 | 0.438 | 0.000 | 0.080 |
| 500 | 0.238 | 0.293 | 0.074 | 0.038 |
| 1000 | 0.470 | 0.148 | 0.143 | 0.034 |
| 2000 | 0.934 | 0.148 | 0.273 | 0.150 |
| 4000 | 2.052 | 0.765 | 0.490 | 0.354 |
| 6000 | | 1.439 | 0.694 | 0.530 |
| 8000 | | | | 0.680 |
| | 61.2 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.793 | | 43.8 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.446 | |
| 1 | 0.000 | 0.325 | 0.000 | 0.131 |
| 500 | 0.169 | 0.184 | 0.133 | 0.010 |
| 1000 | 0.340 | 0.048 | 0.264 | 0.104 |
| 2000 | 0.677 | 0.192 | 0.527 | 0.319 |
| 4000 | 1.334 | 0.642 | 1.090 | 0.697 |
| 6000 | 2.186 | 1.046 | 1.728 | 1.042 |
| 8000 | | 1.541 | | 1.490 |
| | 6.1 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.627 | | 35.3 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.370 | |
| 1 | 0.000 | 0.095 | 0.000 | 0.190 |
| 500 | 0.075 | 0.022 | 0.102 | 0.011 |
| 1000 | 0.146 | 0.048 | 0.206 | 0.025 |
| 2000 | 0.282 | 0.178 | 0.420 | 0.150 |
| 4000 | 0.527 | 0.401 | 0.889 | 0.510 |
| 6000 | 0.754 | 0.580 | 1.395 | 0.880 |
| 8000 | | 0.731 | | 1.278 |
| | 2.4 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.563 | | 84.7 mole % $C_{10}H_{12}O_2$ log $t_0$ = 0.370 | |
| 1 | 0.000 | 0.105 | 0.000 | 0.410 |
| 500 | 0.072 | 0.031 | 0.195 | 0.285 |
| 1000 | 0.141 | 0.036 | 0.394 | 0.159 |
| 2000 | 0.271 | 0.160 | 0.813 | 0.110 |
| 4000 | 0.495 | 0.358 | 1.760 | 0.669 |
| 6000 | 0.683 | 0.509 | 2.800 | 1.283 |
| 8000 | | 0.622 | | 2.018 |

[6] The viscosities at atmospheric pressure $t_0$ cannot be compared for those mixtures for which different falling-weights were used for different concentrations. This was the case for the eugenol carbon disulphide mixtures; two viscometers with different falling-weights were used.

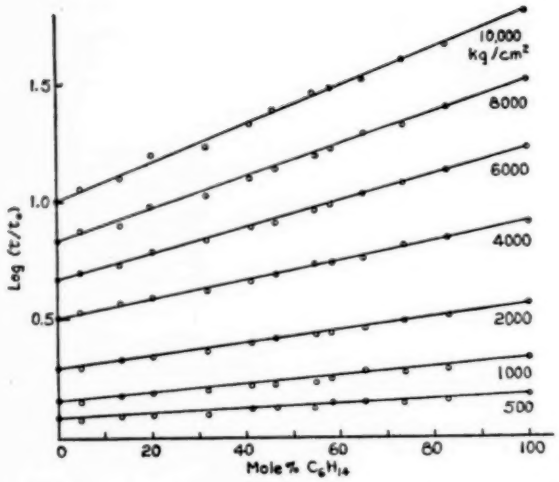


FIG. 1. Relative viscosity at 30° of *n*-hexane carbon disulphide against concentration.

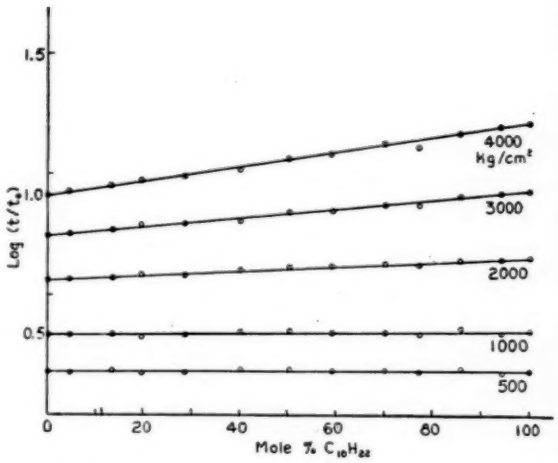


FIG. 2. Relative viscosity at 30° of *n*-hexane *n*-decane against concentration.

slipping over each other. Raman and Krishnan[7] from their studies on birefringence have considered that there is a tendency for nonspherical molecules to orientate under mechanical stress within a liquid; moreover, such an arrangement is most probable for a statistical energy distribution.

Increase of pressure at constant temperature could not be expected to cause any irregularity in the orientation; rather, it should increase the uniformity of it. Bridgman's[8] comment on this point is applicable to the present results: "Along with the idea of molecules with shape goes the conception that at high pressures these shapes must be forced more or less to adapt themselves to each other; in other words, the molecules must begin to show traces of regular arrangement. The regularity is by no means the thorough-going regularity of a crystal in which the molecules are permanently moored to certain mean positions, the molecules of the liquid still circulate about among each other, but as they slide past each other there may be a growing tendency at higher pressures to point the long axes in the direction of relative motion, for example. This increasing order of arrangement seems not only natural, but inevitable at high pressures." Increase of temperature would tend to break up the parallel orientation by increasing the thermal agitation. Under these conditions, the interlocking of molecules probably takes place in a simple way.

There have been several equations proposed for the viscosity of binary mixtures of chemically indifferent liquids

$$\eta = \eta_1^{x}\eta_2^{(1-x)}, \text{ Arrhenius.}^{9} \quad (1)$$

$$\eta = \eta_1 x + \eta_2(1-x), \text{ Kendall and Monroe.}^{10} \quad (2)$$

$$\varphi = \varphi_1 x + \varphi_2(1-x), \text{ Bingham.}^{11} \quad (3)$$

$$\eta = \eta_1 + (\eta_2-\eta_1)K_2a_2Z_m/K_1a_1(1-Z_m) + K_2a_2Z_m, \text{ Ishikawa.}^{12} \quad (4)$$

$$\varphi = \varphi_1 a + \varphi_2 b - K(a-m)(v_1-v_2), \text{ Bingham and Brown.}^{13} \quad (5)$$

$$\log \eta = m \cdot \log \eta_1 + (1-m) \log \eta_2 - \int (q_m/R \cdot T^2)dT, \text{ Lederer.}^{14} \quad (6)$$

$$L_m = xL_a + (1-x)L_b$$

$$L_m' = xL_1' + (1-x)L_2' + Cx(1-x), \text{ Cragoe.}^{15} \quad (7)$$

In these formulae, $\eta$ is the viscosity of the mixture, $\varphi$ the fluidity, $\eta_1$, $\eta_2$, $\varphi_1$, $\varphi_2$, the viscosities and fluidities, respectively, of the components. It has been usual to consider $x$ as the volume,

[7] C. V. Raman and K. S. Krishnan, Phil. Mag. **5**, 767 (1928).
[8] P. W. Bridgman, Proc. Am. Acad. **42**, 111 (1913).
[9] S. Arrhenius, Zeits. f. physik. Chemie **1**, 285 (1887).
[10] J. Kendall and K. P. Monroe, J. Am. Chem. Soc. **39**, 1802 (1917).
[11] E. C. Bingham, J. Am. Chem. Soc. **35**, 195 (1906).
[12] T. Ishikawa, Bull. Chem. Soc. Jap. **4**, 5 (1929).
[13] E. C. Bingham and D. F. Brown, J. Rheology **3**, 95 (1932).
[14] E. L. Lederer, Kolloid-Bei. **34–35**, 270 (1932).
[15] C. S. Cragoe, Proc. World Petroleum Congress, London **F**, 529 (1933).

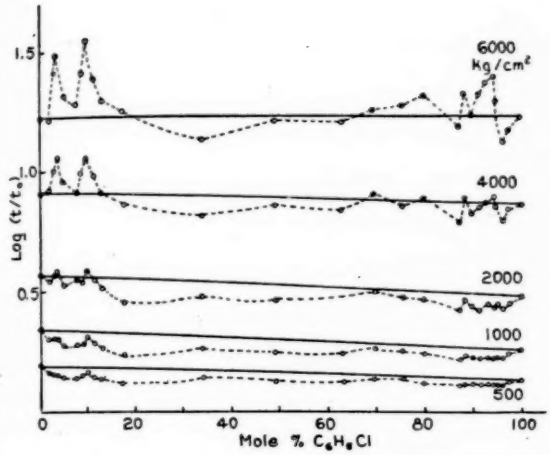


FIG. 3. Relative viscosity at 30° of *n*-hexane chlorobenzene against concentration.

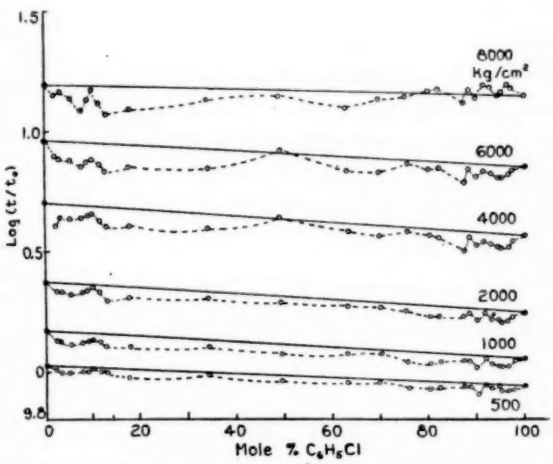


FIG. 4. Relative viscosity at 75° of *n*-hexane chlorobenzene against concentration.

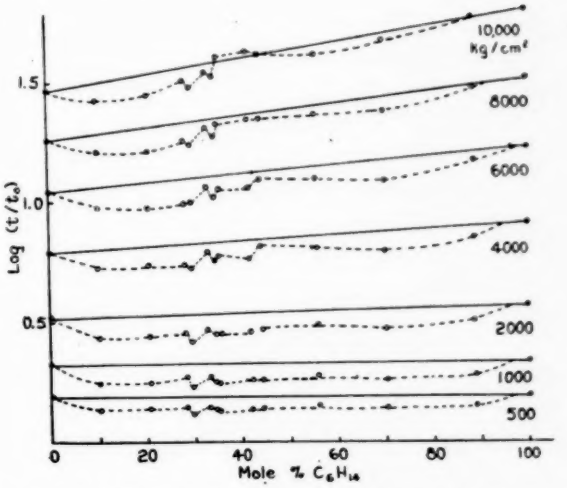


FIG. 5. Relative viscosity at 30° of *n*-hexane diethyl ether against concentration.

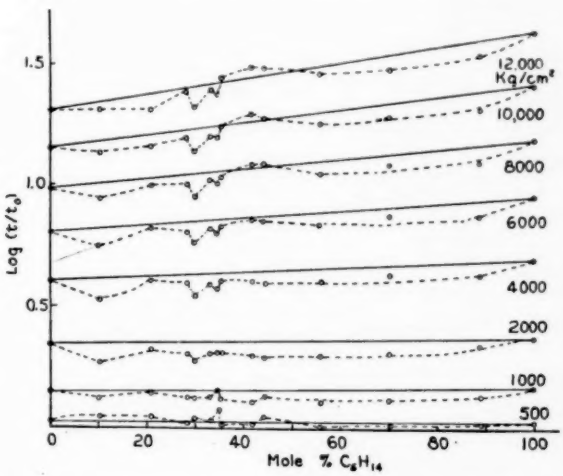


FIG. 6. Relative viscosity at 75° of *n*-hexane diethyl ether against concentration.

weight and molar fractions, indiscriminately. For an explanation of the other symbols used in Eqs. (4) to (7) the reader is referred to the original papers.

The two mixtures of the first group, *n*-hexane carbon disulphide and *n*-hexane *n*-decane, obey Arrhenius' empirical equation of mixture. In these cases, the pressure and temperature coefficients of viscosity of the components are additive in mixture, assuming no relative change in concentration with pressure and temperature change, for since

$$\eta = \eta^{x}\eta^{(1-x)},$$
$$\log_e \eta = x \log_e \eta_1 + (1-x) \log_e \eta_2,$$

and $1/\eta\, d\eta/dp = x/\eta_1(d\eta_1/dp) + 1 - x/\eta_2(d\eta_2/dp)$; also, $1/t\, d\eta/dt = x/\eta_1(d\eta_1/dt) + 1 - x/\eta_2(d\eta_2/dt)$.

Consequently, it seems probable that the simple picture of interlocking of the long, similarly orientated molecules in these mixtures has some validity for one would not expect this type of interlocking to vary much with the concentration.

The log viscosity curves[16] of *n*-hexane diethyl

[16] Dotted lines have been drawn through the computed points while the solid straight lines in the figures represent the behavior of a mixture in which the pressure and temperature coefficients of viscosity of the components are additive. It is convenient to use these lines as bases of reference for the discussion of the actual curves.

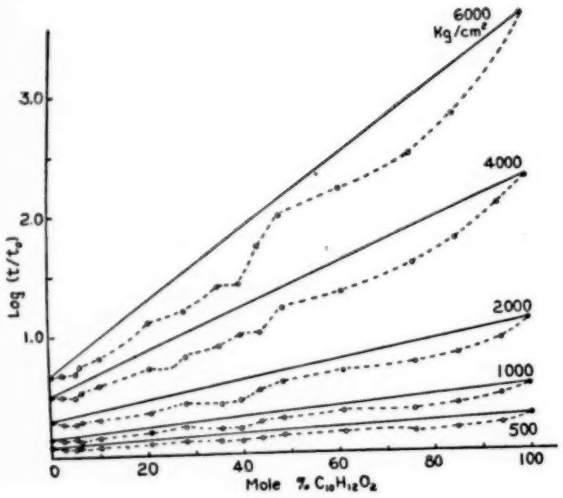


FIG. 7. Relative viscosity at 30° of eugenol carbon disulphide against concentration.

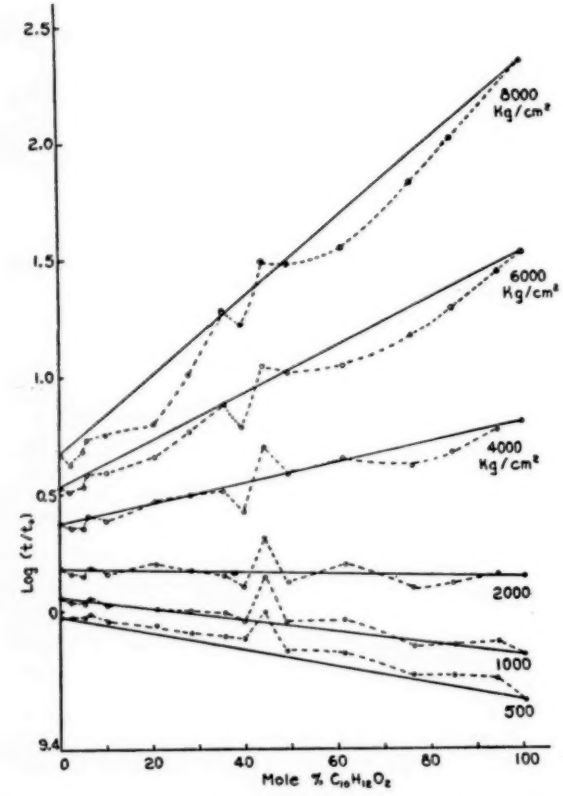


FIG. 8. Relative viscosity at 75° of eugenol carbon disulphide against concentration.

ether, *n*-hexane chlorobenzene, *n*-pentane benzene, and eugenol carbon disulphide display various kinds of irregularities which are in no way similar for these mixtures. For example, the

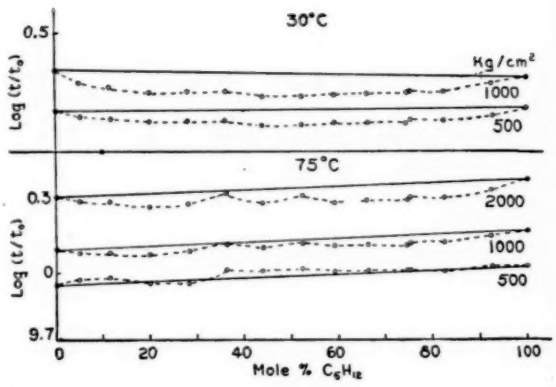


FIG. 9. Relative viscosity at 30° and 75° of *n*-pentane benzene against concentration.

peaks in the hexane chlorobenzene isobars do not appear on the corresponding pentane benzene curves; also, the same curves for hexane ether exhibit distinctive complexities. Inasmuch as these mixtures of the second group, with the exception of pentane benzene, contain a polar component, it is possible that complexes or associations of molecules will affect the results. Although the effects of association, as judged by the departures of the density-concentration curves from linearity do not seem to be significant for the viscosity of the mixtures at atmospheric pressure, the effects at high pressures may play important parts in the observed viscosity. While the final free space arrangement of the molecules depends little on whether the molecules are in a combined or free state, it is clear that the effect on viscosity will be different, for the mechanism of viscous resistance involves relative motion of interlocked structures which in turn will depend on the molecules of the mixtures.

Bridgman[17] in discussing association as applied to his results on water at high pressures prefers to leave open the question of whether pressure increases or decreases the amount of association, although his results suggested that pressure merely influenced the effects of association without necessarily changing the amount. Collins,[18] from an investigation of the infrared absorption spectra of liquids known to associate, concludes that his results indicated no change in association

[17] P. W. Bridgman, Proc. Am. Acad. **47**, 546 (1912).
[18] J. R. Collins, Phys. Rev. **39**, 305 (1930).

with change of pressure. Whether or not the degree of association changes with pressure, the effect of association apparently changes with pressure, becoming stronger with increase of pressure and consequently complicating the interlocking.

From these considerations it appears probable that the interlockings in this group of mixtures are complicated by the structural differences of the component molecules and their effects. Thus the observed complexities in the viscosity isobars, Figs. 3 to 9 inclusive, are unique functions of mixture and they display such bewildering variations with concentration that it seems hopeless to attempt to express the viscosity at high pressures by a quantitative relation. It may be stated that the irregularities observed in the viscosity are of such magnitudes that it is impossible to consider them as due to experimental errors.

The results for the *n*-pentane benzene mixtures are significant. While these mixtures might be classed with those in the first group, since all are composed of nonpolar components, it is evident, however, from an inspection of Fig. 9 that the interlocking must be quite different. The departures of the viscosity isobars from linearity at 30° are in the nature of sags which extend uniformly over the concentration range and which vary greatly with pressure. But at 75°, the sags are much different, being absent or less in amount at the corresponding pressures; however, at the highest pressure, the qualitative natures of the curves become more nearly similar to those at 30°. There is no reason for abnormality in the pentane benzene mixtures due to such effects as previously discussed and the interlocking would be thought characteristic of the component molecules.

A complete explanation of the sags in the viscosity isobars of the *n*-pentane benzene mixtures would necessitate more exact information about viscous interlocking. Yet, it does not seem unlikely that a change in orientation with change of pressure, effected in such a way that there is a tendency for the flat planes of the benzene molecules to become parallel with the direction of relative motion, might conceivably result in an interlocking not unlike that which has been considered in the first group of mixtures. This particular type of interlocking in pentane benzene mixtures offers a qualitative explanation of a relative viscosity less than that obtained if the pressure and temperature coefficients of viscosity of the components were additive in mixture.

## Conclusions

The log viscosity for two mixtures, *n*-hexane carbon disulphide and *n*-hexane *n*-decane at different pressures and temperatures, has been shown to obey Arrhenius' equation for the viscosity of a binary mixture, indicating that the pressure and temperature coefficients of viscosity of the components are additive. It is believed that a comparatively simple type of interlocking occurs in these mixtures due to the effectively linear structure of the molecules and the absence of non-uniform molecular fields such as would cause some sort of association. For the mixtures *n*-hexane diethyl ether, *n*-hexane chlorobenzene, *n*-pentane benzene, and eugenol carbon disulphide, few generalities can be stated about association of molecules and the resulting kinds of interlocking at high pressures for they are specific properties of mixture.

The viscosity of liquids is not at all well understood notwithstanding the theoretical advances of Raman[19] and Andrade.[20] While the viscosity of liquids at high pressures represents somewhat unusual experimental conditions, nevertheless it displays those salient features of structure which exist in liquids at more normal conditions but which probably are less effective in the comparatively large "free-space." Considering the results of this investigation, viscosity is a specific property of the molecule and as such it offers prohibitive difficulties for any complete, theoretical generalizations at present.

This problem was suggested to the author by Professor P. W. Bridgman and it is a pleasure to acknowledge his interest and cooperation.

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[19] C. V. Raman, Nature **3**, 532 (1923); **3**, 600 (1923).
[20] E. N. da C. Andrade, Phil. Mag. **17**, 497 (1934), and **17**, 698 (1934).

# Errata: The Flow Characteristics of Sewage Sludge and Other Thick Materials

WILHELM MERKEL, *Stuttgart*

(Physics **5**, 355, 1934)

IN Fig. 2 of this paper there are some changes. The correct figure is published here.

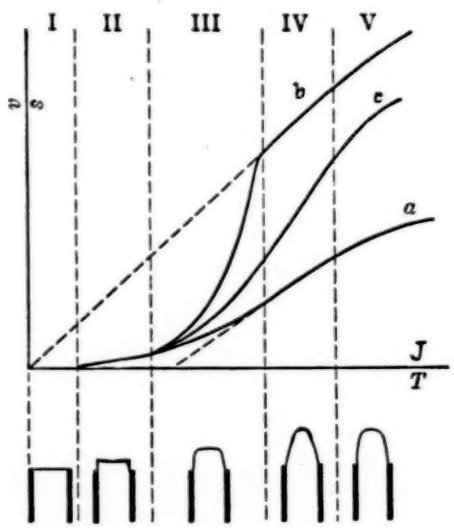


FIG. 2. The five types of flow of plastic bodies. Velocity distribution over bore of tubes. $v$ and $J$ are velocity and gradient in the tube. $s$ and $T$ are the shear and torque in the rotation viscometer. The lower part of figure shows variation in velocity across the pipe section.